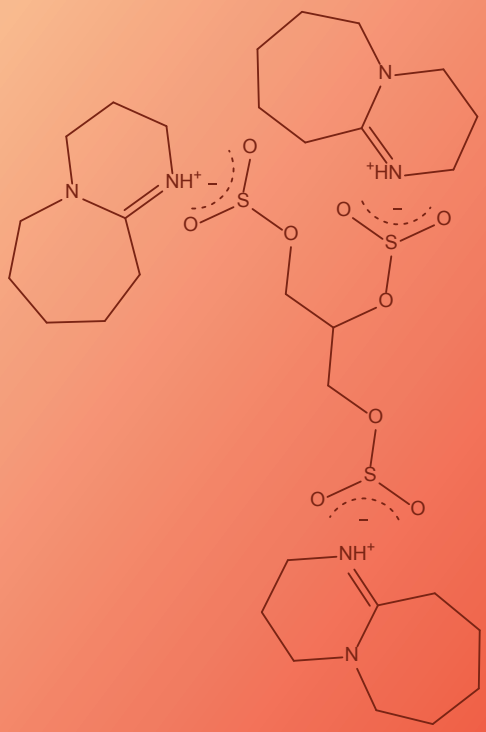
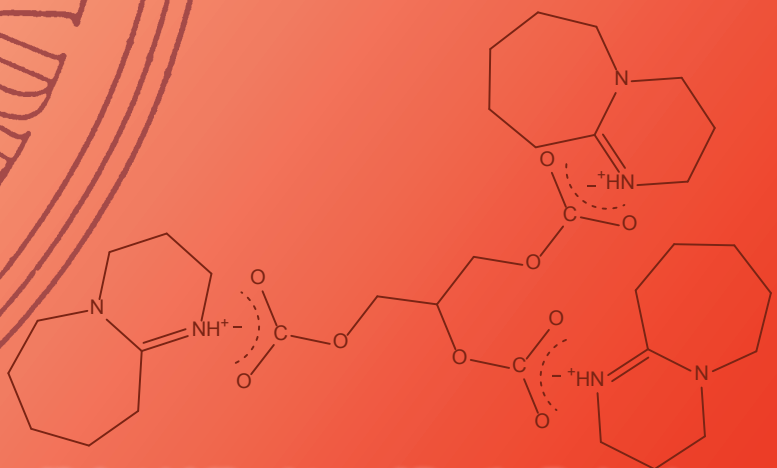
Towards Optimal Fractionation of Lignocellulosic Biomass Using Switchable Ionic Liquids



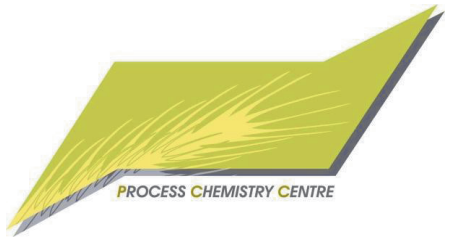
Ikenna Anugwom



Laboratory of Industrial Chemistry and Reaction Engineering
Process Chemistry Centre
Department of Chemical Engineering
Åbo Akademi University
Turku/Åbo 2014

Towards Optimal Fractionation of Lignocellulosic Biomass Using Switchable Ionic Liquids

IKENNA ANUGWOM



Laboratory of Industrial Chemistry and Reaction Engineering
Process Chemistry Centre
Department of Chemical Engineering
Åbo Akademi University
Turku/Åbo 2014

Supervised by

Professor Jyri-Pekka Mikkola
Laboratory of Industrial Chemistry and Reaction Engineering
Process Chemistry Centre
Department of Chemical Engineering
Åbo Akademi University
Finland
Technical Chemistry
Department of Chemistry
Chemical-Biological Centre
Umeå University
Sweden

Reviewers

Prof. Lars Berglund
Fiber and Polymer Technology
Royal Institute of Technology, KTH
Stockholm, Sweden
and

Dr. Mihkel Koel
Lead research scientist
Tallinn University of Technology
Tallinn Estonia

Opponent

Prof. Lars Berglund
Fiber and Polymer Technology
Royal Institute of Technology
Stockholm, Sweden

ISBN 978-952-12-3030-1
Painosalama Oy – Turku, Finland 2014

This work is dedicated to Eng. Christopher Mbanefo Anugwom

Daddy hope I made you proud?

PREFACE

The present work was carried out at the Laboratory of Industrial Chemistry and Reaction Engineering, Process Chemistry Centre, Department of Chemical Engineering, Åbo Akademi University between 2009 and 2014. Main part of the work was funded by the Finnish Bioeconomic Cluster (FIBIC) and the Finnish Funding Agency for Technology and Innovation (TEKES). This research work is also a part of the activities of Process Chemistry Centre (PCC) a centre of excellence financed by Åbo Akademi University.

I would like to express my profound gratitude to Professor Jyri-Pekka Mikkola for introducing me into the benign world of ionic liquids and for the opportunity to try new things like 'switches and twitches', also for sharing his scientific enthusiasm and experiences. I am also grateful to Professor Tapio Salmi of the chance to work in such a vivid and dynamic laboratory.

I would like to express my heart felt gratitude to Docent Päivi Mäki-Arvela for her energetic participation and supervision in the everyday research work. Special thanks to the co-authors in my publications; Dr. Pasi Virtanen, Dr. Valerie Eta for their immeasurable assistance and advice, Dr. Mattias Hedenström, Dr. Manu Lahtinen, Dr. Micheal Hummel and Dr. Pia Damlin for their contribution in the production of the publications as well as Professors Herbert Sixta and Stefan Willför. Prof.em. Rainer 'Panco' Sjöholm and M.Sc. Päivi Pennanen were invaluable in terms of the NMR studies. Docent Kari Eränen is gratefully acknowledged for his efforts and expertise in the experimental set-up. I am deeply indebted to Sebastian von Schoultz for showing me the ins and outs in carbohydrate analysis carried out at the Department Wood and Paper Chemistry of Åbo Akademi. With high regards I would like to thank all the past and present colleagues at the laboratory for the nice working atmosphere.

I am using this opportunity to express my sincere appreciation to my sweet mother Mrs. Lucy Anugwom, to my big brother Nomso (sonnic) Anugwom, also to my small brother Chigozie (Chi-boy) Anugwom and to our baby sister Uju (Titi) Anugwom Oragwu, John (sha) Madukwe and their families.

Finally, to my angels my daughters you are the reason daddy wakes up every day thank you. Soili, my soul, my rock, I will do it again as long as you are with me. Thank you for your love encouragement and for everything.

Ikenna Anugwom

Åbo,

ABSTRACT

Ikenna Anugwom

Towards Optimal Fractionation of lignocellulosic Biomass using Switchable Ionic Liquids

Doctoral Thesis, Laboratory of Industrial Chemistry and Reaction Engineering, Process Chemistry Centre, Department of Chemical Engineering, Åbo Akademi University 2014.

Keywords: Switchable Ionic Liquids (SILs), Fractionation, selective extraction, delignification, enrichment, Crystallinity, Mild treatment, Effective fibrillation, Organic superbase, alkanol amine.

New types of switchable ionic liquids (SILs), containing 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU), glycerol and an acid gas (CO_2, SO_2), were easily synthesized and characterized. The [DBU][Carbonate] or [sulfonate] were synthesized from a non-ionic mixture of molecular organic polyol and amidine base upon bubbling of an acid gas (CO_2, SO_2). Moreover, they were switched back to the original molecular solvents by flushing out the acid gas (CO_2, SO_2) by heating and/or bubbling with an inert gas such as N_2 through it. The structures of the SILs were confirmed by NMR and FTIR. The change from low polarity (molecular) solvent to high polarity (Switchable Ionic Liquid, SIL) was also indicated by the changes in properties, such as viscosity and miscibility with different organic solvents. The decomposition temperatures of the SILs were determined by means of Thermo Gravimetric Analysis (TGA) and gave values in the range of 50°C and 120°C for DBU-glycerol-CO_2-SIL and DBU-glycerol-SO_2-SIL, respectively. Due to the relatively high decomposition temperatures, these novel SILs can be employed in multiple applications.

SILs made from alcohols, either hexanol or butanol, and CO_2 together with an amidine DBU) were investigated as dissolution/fractionation solvents for wood material. Both native spruce (*Picea abies*), and pre-extracted spruce were treated with either DBU-butanol-CO_2-SIL or DBU-hexanol-CO_2-SIL for 5 days at 55°C under normal pressure. After the treatment time (5 days), the undissolved fraction contained 38 wt-% less hemicelluloses compared to native spruce. There was an increase in the glucose content of the milled spruce treated with both SILs, since the milling step reduced the cellulose crystallinity of the wood and facilitated an easier SIL access into the wood. The solvents

were very neutral in terms of lignin removal. Consequently, only about 2% of the lignin was removed from native wood. Moreover, a priori removal of the wood extractives did not influence the lignin removal.

As another case, SILs synthesised from glycerol and industrial flue gas (CO_2) together with an amidine (DBU) was used as fractionation solvents for lignocellulosic material. Fresh birch wood (*Betula Pendula*) was treated with SIL for either 1 or 5 days at 100°C under atmospheric pressure. After the dissolution of birch in SIL, the undissolved fraction contained 25 wt-% less hemicelluloses compared to the native birch. Furthermore, its lignin content decreased by 11 wt-%. The undissolved wood fibrillated became loosely bounded, and contained about 55 wt-% of cellulose. Up to 76 wt-% of the recovered materials from the spent SIL were hemicelluloses, mainly xylan. The spent SILs were reused for fresh wood dissolution for four consecutive cycles and in each time the wood dissolution was almost equally efficient.

Furthermore, an unorthodox and feasible fractionation method of birch chips (*B. pendula*) using an alkanol amine (monoethanol amine, MEA) and an organic super base (DBU) derived SILs with two different triggers CO_2 and SO_2, was studied. After the SIL treatment, the dissolved fractions were selectively separated out by a step-wise method using an anti-solvent to induce precipitation. The SIL was recycled after concentration and evaporation of the added molecular solvents (i.e. anti-solvent). The undissolved wood after DBU-MEA-SO_2-SIL treatment contained 80 wt-% cellulose, 10 wt-% hemicelluloses, and 3 wt-% lignin, whereas DBU-MEA-CO_2-SIL treatment resulted in 66 wt-% cellulose, 12 wt-% hemicelluloses and 11 wt-% lignin, respectively.

Two-step treatment of birch chips was carried out using diethanolamine (DEA), DBU and CO_2 and forming (DBU-DEA-CO_2-SIL), resulting in 23 wt-% reduction in 24 h. The chips reduced to 32 wt% of their initial weight after two consecutive treatments with fresh SIL in 24 h. The relative amount of wood lignin reduced from 20 wt-% to 14 wt-% upon two treatment cycles. The relative amount of cellulose in the undissolved fraction after SIL treatment increased from 42 wt-% to 61wt-% after the second cycle, and cellulose was efficiently fibrillated. The dissolved materials recovered from spent SIL after treatments were rich in xylan, corresponding to about 90 wt-% of the total amount of hemicelluloses. The xylan represented 85 wt-% of the recovered material. The XRD

results revealed that the crystallinity of the undissolved material increased slightly, indicating dissolution of the amorphous material. Moreover, transformation of cellulose form I to form II was not observed.

Optimal fractionation process conditions for wood dissolution with switchable ionic liquid were determined. The Short-Time-High-Temperature (STHT) system for fractionation of woody biomass using SILs based on DBU and MEA with SO_2 was introduced as a selective and efficient way to extract components from lignocellulosic material. The undissolved wood chips treated with the SIL were fibrillated. A selective dissolution of mainly lignin was achieved by this system using SIL at 160°C for 2 h in the STHT system. All dissolution experiments of wood were performed using air dried wood sample, containing about ~5 wt-% moisture. Both hard-and softwood were fractionated into their major fractions under a rather short time with the SIL-water mixture as a solvent and with a weight ratio of 5:3:1 (SIL:water:wood). About 95 wt-% of the lignin was extracted from the wood chips into the solvent. The dissolved components in the spent SIL were recovered by the addition of an anti-solvent and over 70 % of the dissolved components were recovered. The recovered material from the spent SIL consisted of 19 wt-% hemicellulose, while the rest of the material was mainly lignin. The undissolved fluffy material recovered after the treatment time contained mainly a cellulose rich pulp, with ~70 wt-% cellulose and ~20 wt-% hemicellulose.

REFERAT

Fraktionering av lignocellulosamaterial med hjälp av reversibla joniska vätskor

Doktorsavhandling, Laboratoriet för teknisk kemi och reaktionsteknik, Processkemiska centret, Institutionen för kemiteknik, Åbo Akademi, 2014

Nyckelord: reversibla joniska vätskor (SIL), fraktionering, selektiv extraktion, delignifiering, anrikning, kristallinitet, mild behandling, effektiv fibrillering, organisk superbas, alkanolamin

En ny familj av reversibla (switchable) joniska vätskor (SIL) innehållande 1,8-diazobicyklo-[5.4.0]-undek-7-en (DBU), en molekyl innehållande en eller flera hydroxyl-grupper (t.ex. glycerol) och en sur gas (CO_2, SO_2) syntetiserades via en enkel procedur samt karakteriserades. [DBU][karbonat] eller [sulfonat] bildades ur en respektive icke-jonisk blandning av en molekylär, organisk polyol (eller ennan molekyl innehållande en OH-grupp) och en amidinbas under bubblandet av en sur gas. Därtill kunde den joniska vätskan omvandlas tillbaka till sina beståndsdelar med hjälp av att upphetta och/eller bubbla en inert gas såsom kväve genom vätskan. SIL- strukturerna kartlades med bl.a. NMR- och FTIR- spektroskopi. Omvandlingen från lågpolära (molekylära) vätskor till högpolära joniska vätskor (SIL) bekräftades även genom att observera förändringar i deras fysikaliska egenskaper, såsom viskositet och färg. Nedbrytningstemperaturerna hos SILs bestämdes med hjälp av termogravimetrisk analys (TGA) som antydde att nedbrytningstemperaturen hos de syntetiserade föreningarna log mellan 50 (DBU-1-butanol-CO_2-SIL) och 200^{o}C (DBU-MEA-SO_2-SIL). De nya joniska vätskorna uppvisade högre nedbrytningstemperaturer jämfört med i tidigare litteraturen förekommande exempel och kunde därför tillämpas på flera ändamål.

Utöver de ovannämnda exemplen, även reversibla (switchable) joniska vätskor uppbyggda av bl.a. alkoholer, antingen hexanol eller butanol, och CO_2 samt en amidin (DBU) användes vid upplösning och fraktionering av ved, både för naturligt granmaterial (*Picea Abies*) och för granmaterial ur vilket extraktivämnen hade avlägsnats *a priori*. I detta fall behandlades gran med DBU-alkohol-CO_2-SIL som bildades ur en ekvimolär

blandning av antingen 1-hexanol eller 1-butanol och DBU (samt en sur gas). Blandningens viskositet ökade därmed från 7.1 mPas till 2980 mPas för DBU-hexanol-CO_2-SIL samt från 5.1 till 1600 mPas för den respektive DBU-butanol-CO_2-SIL (vid rumsemperatur). Efter behandling (i fem dagar) innehöll den olösta fraktionen 38 vikt-% mindre hemicellulosor jämfört med den naturliga granen. Glukoshalten ökade markant både för ett prov av malen, kvarnbehandlad gran samt för industriell flis. Den malna veden uppvisade som förväntat en lägre kristallinitet av cellulosan och joniska vätskor kunde då lättare penetrera vedmaterialet. Alla syntetiserade joniska vätskor visade sig vara relativt neutrala i avseende på upplösning och avlägsnandet av lignin. Slutligen endast ca. 2 % av lignin avlägsnades ur det naturliga vedmaterialet i detta fall. Därtill observerades det att extraktivämnena inte nämnvärt påverkade ligninborttagningen.

Joniska vätskor syntetiserade ur glycerol och sura gaser (CO_2 m.m.) tillsammans med amidiner (t.e.x. DBU) användes även för fraktionering av andra lignocellulosor: färsk björk (*Betula pendula*) utsattes för behandling, för en period på en till fem dagar vid 100^{o}C under atmosfäriskt tryck. Efter upplösning av björk i SIL innehöll den olösta fraktionen 25 vikt-% mindre hemicellulosor jämfört med naturlig björk. Samtidigt sjönk provets ligninhalt med 11 vikt-%. Det olösta, fibrillerade vedmaterialet blev lösbundet samt innehöll ca. 55 vikt-% cellulosa. Cirka 76 vikt-% av det tillvaratagna materialet bestod av hemicellulosor, huvudsakligen xylan. Joniska vätskor som hade redan använts för fraktionering återanvändes för upplösning av färsk ved i fyra konsekutiva omgångar och vid varje cykel var resultatet praktiskt taget lika bra.

Vid nästa steg studerades en ny samt ekonomiskt lovande metod för upplösning av björkflis (*Betula pendula*) i form av att använda en SIL framställd ur en alkanolamin (monoetanolamin, MEA), en organisk superbas (1,8-diazabicyklo-[5.4.0]-undek-7-en, DBU) samt två olika sura gaser, CO_2 och SO_2. Efter SIL behandlingen separerades de upplösta fraktioner genom att tillämpa en stegvis metod med tillsättandet av ett anti-lösningsmedel för att få en utfällning till stånd. SIL återcirkulerades efter koncentrering (vakuumbehandling). Det olösta vedmaterialet som isolerades efter DBU-MEA-SO_2-SIL behandlingen innehöll 80 vikt-% cellulosa, 10 vikt-% hemicellulosor samt 3 vikt-%

lignin, medan materialet efter DBU-MEA-CO_2-SIL behandlingen gav material med 66 vikt-% cellulosa, 12 vikt-% hemicellulosor och 11 vikt-% lignin. Resultaten tyder på att DBU-MEA-CO_2-SIL var fyra gånger mera effektivt jämfört med DBU-MEA-CO_2-SIL samt också ett bättre lösningsmedel för borttagning av lignin.

Tvåstegsbehandling av industriell björkflis utfördes med SIL bestående av dietanolamin (DEA), DBU och CO_2 (DBU-DEA-CO_2-SIL). Med hjälp av denna joniska väska kunde en viktförminskning på 23 vikt-% observeras efter 24 timmar. Flisvikten minskade med 32 vikt-% jämfört med dess ursprungliga vikt efter två konsekutiva behandlingar med färsk SIL i 24 timmar. Den relativa ligninmängden minskade från 20 vikt-% till 14 vikt-% i två konsekutiva behandlingar. Däremot ökade den relativa cellulosamängden i den olösta fraktionen efter SIL-/behandlingen från 43 vikt-% till 61 vikt-% efter den andra cykeln och cellulosan blev effektivt fibrillerad. Det lösta materialet, som återvanns ur den använda joniska vätskan efter behandlingen, innehöll mycket xylan: detta utgjorde ca. 90 vikt-% av den totala mängden hemicellulosor. Xylanhalten i det återvunna materialet var 85 vikt-%. Resultaten ur röntgendiffraktion (XRD) antydde att det olösta materialets kristallinitet ökade något samt bekräftade hypotesen om att det amorfa materialet hade löst sig. Däremot observerades ingen omvandling av cellulosa I till cellulosa II.

Optimala fraktioneringprocessbetingelser för ved med reversibla joniska vätskor kartlades. Fraktionering av vedbiomassa med dessa joniska vätskor uppvisade sig att vara en selektiv och effektiv metod för extraktion av olika komponenter från lignocellulosa. Den olösta fraktionen hos en vedflis fibrillerades. Selektiv upplösning av huvudsakligen lignin förverkligades då behandlingen utfördes vid 160 ^{o}C under två timmars tid. De flesta experiment utfördes för lufttorkade vedprov som innehöll ca. 5 vikt-% fukt. Både barr och lövved fraktionerades till respektive huvudfraktioner under en relativt kort tid genom att använda en SIL-vattenblandning med ett viktförhållande 5:3:1 SIL (jonisk vätska, vatten och ved). Cirka 95 vikt-% av ligninet extraherades ur vedflis till den joniska vätskan. De lösta komponenterna i den joniska vätskan kunde regenereras genom tillsättning av en antilösningsmedel varvid ca. 70 vikt-% av de lösta komponenterna återvanns. Fällningen innehöll 19 vikt-% hemicellulosor, medan resten av materialet huvudsakligen bestod av lignin. De olösta, fluffiga flisresterna innehöll huvudsakligen en cellulosarik massa med 70 vikt-% cellulosa och 20 vikt-% hemicellulosa.

LIST OF PUBLICATIONS

The thesis consists of following Publications, which are referred to in the text by their roman numerals. Papers I-VII is enclosed in the Appendix.

I Anugwom, I., Mäki-Arvela, P., Virtanen, P., Damlin, P., Mikkola, J.-P., Switchable ionic liquids (SILs) based on glycerol and acid gases, *RSC Advances*, **2011**, *1*, 452-457

II Virtanen, P., Anugwom I., Mikkola, J.-P., Mäki-Arvela, P., Method for Fractionating of Lignocellulosic Material and Novel Ionic Liquids Thereof, **2010**, FI20106142, PCT/FI2011/050959

III Anugwom, I., Mäki-Arvela, P., Virtanen, P., Willför, S., Sjöholm, R., Mikkola, J.-P., Selective Extraction of Hemicelluloses from Spruce Flour using Switchable Ionic Liquids, *Carbohydrate Polymers*, **2012**, *87*, 2005-2011

IV Anugwom, I., Mäki-Arvela, P., Virtanen, P., Willför S., Damlin P., Hedenström M., Mikkola J.-P., Treatment of birch wood by a switchable ionic liquid based on 1,8-diazabicyclo-[5.4.0]-undec-7-ene-glycerol carbonate, *Holzforschung*, **2012**, *66,809-815*.

V Anugwom, I., Eta, V.,Mäki-Arvela, P., Virtanen, P., Hedenström M., Hummel, M., Sixta, H., Mikkola J.-P., Novel Alkanol Amine-organic Superbase derived Switchable Ionic Liquid(SIL) as a Delignification solvent for Birch (B.Pendula). *ChemSusChem*, (in press), Dio:10.1002/cssc.201300773.

VI Anugwom, I., Eta, V.,Mäki-Arvela, P., Virtanen, P., Hedenström M., Ma, Y., Hummel, M., Sixta, H., Mikkola J.-P., Towards optimal selective fractionation for Nordic woody biomass using Novel Amine–Organic Superbase derived Switchable Ionic Liquid (SIL). (submitted)

VII Anugwom, I., Eta, V., Mäki-Arvela P., Virtanen, P., Lahtinen, M., Mikkola J.-P., The composition and crystallinity of Birch Chips (*Betula Pendula*) upon 'DBU-DEA-CO_2-SIL' alkanol amine–organic superbase-derived Switchable Ionic Liquid (SIL) treatment, *Green Process and Synthesis* (in press) Dio: 10.1515/gps-2013-0108.

AUTHOR'S CONTRIBUTION

All the experiments were planned and carried out by the author, except SEM, DSC, GPC, NMR, XRD measurements. All the first drafts of the manuscripts were written by the author and finalized together with the supervisors.

OTHER CONTRIBUTIONS RELATED TO THE TOPIC

Anugwom I., Mäki-Arvela P., Salmi T., Mikkola J.-P., Ionic liquids Assisted Extraction of Nitrogen and Sulphur-Containing Air pollutants from Model Oil and Regeneration of Spent Ionic Liquids, *Journal of Environmental protections*, **2011**,2, 796-802

Eta, V., Anugwom, I., Virtanen, P., Eränen, K., Mäki-Arvela, P., Mikkola, J.-P. Loop vs. batch reactor setups in the fractionation of birch chips using switchable ionic liquids. *Chemical Engineering journal*, 2014, 238, 242-248.

Eta, V. Anugwom, I., Virtanen, P., Mäki-Arvela, p.,J.-P. Mikkola,J.-P. Enhanced mass transfer upon switchable ionic liquid mediated wood fractionation: Ind. Crops prod. **2014**, in press

Mäki-Arvela P., Anugwom I., Virtanen P., Sjöholm R., Mikkola J.-P., Dissolution of lignocellulosic materials and its constituents using ionic liquids - A Review, *Industrial Crops & Products*, **2010**, *32*, 175-201

Anugwom I., Mäki-Arvela P., Eta V., Virtanen P., Mikkola J.-P., Short Time High Temperature (STHT) System using Alkanol amine -Superbase Ionic Liquid Systems As an Optimal Fractionation Approach, **2013**, 4th International Workshop of COST Action CM0903, Sustainable production of fuels/energy, materials & chemicals from biomass, Valencia, Spain, Oral Presentation.

Anugwom I., Mäki-Arvela P., Eta V., Virtanen P., Mikkola J.-P., Alkanol Amine-organic Superbase derived Switchable Ionic Liquid(SIL) as a Delignification solvent for Birch (B.Pendula): switching with CO_2 vs. SO_2, **2013**, 1st EuCheMS Congress on Green and Sustainable Chemistry, Budapest, Hungary, Oral Presentation.

Anugwom I., Mäki-Arvela P., Eta V., Virtanen P., Mikkola J.-P.,Towards optimal treatment procedure upon fractionation of Nordic lignocelluloses using novel Alkanol amine-superbase ionic liquid system, **2012**, 3rd International Workshop of COST Action CM0903, Sustainable production of fuels/energy, materials & chemicals from biomass, Thessaloniki, Greece, Oral Presentation.

Anugwom I., Mäki-Arvela P., Eta V., Virtanen P., Mikkola J.-P.,Towards optimal treatment procedure upon fractionation of Nordic lignocelluloses using novel Alkanol amine-superbase ionic liquid system, **2012**, *4th Nordic Wood Biorefinary conference*, Helsinki, Finland, book of abstracts

Anugwom I., Mäki-Arvela P., Eta V., Virtanen P., Mikkola J.-P.,A Novel Alkanol amine-Organic Superbase derived Switchable Ionic Liquids as a Fractionation Solvent for Nordic Lignocellulose, **2012**, *4th international IUPAC conference on Green Chemistry*, Foz do Igazu, Brazil, Oral Presentation

Anugwom I., Mäki-Arvela P., Eta V., Virtanen P., Mikkola J.-P., Selective Fractionation of Nordic Lignocellulose Using Novel Alkanol amine-Organic Superbase derived Switchable Ionic Liquid, **2012**, *15th international conference on advances in catalysis for biomass valorization*, Thessaloniki, Greece, book of abstracts.

Anugwom I., Mäki-Arvela P., Virtanen P., Mikkola J.-P., Novel Choline–based Switchable Ionic Liquid for fractionation of lignocellulosic materials, **2011**, *1st international conference on ionic liquids in separation and purification technology*, Sitges, Spain, oral presentation.

Anugwom I., Mäki-Arvela P., Virtanen P., Mikkola J.-P., Utilization of CO_2 as a trigger in the synthesis of novel Switchable ionic liquids for the dissolution of lignocellulosic materials, **2011**, *11th international conference on carbon dioxide utilization*, Dijon, France, book of abstracts.

Anugwom I., Mäki-Arvela P., Virtanen P., Mikkola J.-P., Utilization of Novel Switchable Ionic Liquids for the Fractionation of Lignocellulosic Materials, **2011**, 4th Conference on ionic liquids (COIL-4), Washington D.C, United States, oral presentation.

Anugwom I., Mäki-Arvela P., Salmi T., Mikkola J.-P., Extraction of Nitrogen and Sulfur-containing compounds from Heavy fuel oil by 1-ethyl-3-methyl-imidazolium chloride , **2010**, *EUCHEM Conference on molten salts and ionic liquids*, Bamberg Germany, book of abstracts.

CONTENTS

1. INTRODUCTION

The worldwide demand for energy is continuously growing and, consequently, this leads to higher demand for our dwindling as well as unsustainable supply of petroleum and other fossil resources. Furthermore, the challenges facing mankind in terms of the use of fossil fuels include strong implications towards emergence of the global warming caused by the emission of greenhouse gases from electric power plants, industry and transportation. Thus, a growing interest in terms of a search for alternative sources and more environmentally friendly resources is evident [1, 2]. Lignocellulosic biomass has the potential to serve as a low cost and renewable feedstock for the production of both fuels and biochemicals and, thus, could be a viable replacement for the fossil fuel resources [3-5].

1.1. Lignocellulosics

Lignocellulosic biomass provides an abundant and low costing resource that could support an industrial scale production of fuels and chemicals. It can be divided into four main categories of interest, 1) agricultural residual including raw materials such as corn stover and wheat straw; 2) forestry residual, for example saw dust, branches as well as thinning and mill waste; 3) dedicated energy crops e.g. woody (poplar) or herbaceous (willow); and 4) recycled fibre from society, e.g. waste paper [6].

1.1.1. Wood- a major source of lignocelluloses materials

Wood is a heterogeneous, hygroscopic, cellular and anisotropic material. It is composed of cells, and the cell walls, in turn, are composed of microfibers of cellulose (40% – 50%) and hemicellulose (15% – 25%), supplemented with lignin (15% – 30%) [7]. Furthermore, extractives are present in variable amounts, depending on the species. The main wood categories include hardwoods and softwoods.

Hardwood trees (angiosperms) are usually plants with covered seeds generally having broad leaves. They are abundant in the temperate regions of the world [6] and their wood contains water-conducting cells (tracheids and vessel elements), in addition to tightly-packed, thick-walled fibre cells. Examples of some common hardwood species are various birches (Betula *spp*), maples (Acers *spp*) and beeches (Fagus *spp*).

Softwood trees (conifers or gymnosperms) are usually plants with naked seeds. Furthermore, they are cone bearing and their leaves are scale or needle like. Wood of softwood trees is composed essentially of water-conducting cells (tracheids) without wood fibre cells. Examples of some common softwood species are pines (Pinus *spp*), spruce (Picea *spp*), alders (alnus *spp*) and larch (larix *spp*) [6].

1.1.2. Cellulose

Plant cells are structurally based on cellulose which, therefore, represents the most important natural substance produced by living organisms. Furthermore, cellulose is the most important skeletal component in plants [8]. Cellulose is an almost inexhaustible polymeric raw material available on earth today, exhibiting an interesting structure and valuable properties. In addition, it is the most common organic polymer, which is equivalent to about 1.5×10^{12} tons of biomass produced annually, thus considered to be a vast source of environmental friendly and biocompatible raw materials [9].

Cellulose dominates in many technical products such as in paper, films, fibres and additives. Cellulose is predominantly isolated from wood by the various pulping processes in a large scale.

Cellulose can be described as a linear-polymer glucan with a uniform chain structure, since it consists of anhydroglucopyranose units which are joined to each other by β-(1→4)-glycosidic linkages. Furthermore, the repeating units of cellulose chain are a cellobiose unit which consists of two glucose unit. Cellulose molecules are usually linear and they exhibit strong tendency to form hydrogen bonds. In native form cellulose is linear yet semi-crystalline polymer, having a highly structured crystalline region called microfibrils and also amorphous parts [10].

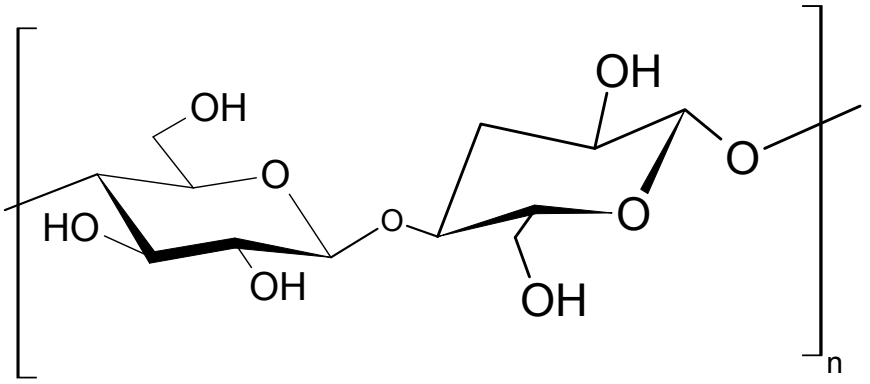


Figure 1. Molecular structure of cellulose (adapted from ref. [11]).

1.1.3. Hemicelluloses

Hemicellulose belongs to the group of heteropolysaccharides which are formed through biosynthetic routes which are different compared to that of cellulose [6, 7, 12]. Hemicelluloses are heterogeneous and they provide the supporting functions in the cell walls, analogously to cellulose. They are built of various sugar units, with shorter molecular chains compared to cellulose, and branching of chain molecules. These sugar units can be further subdivided into several groups such as pentoses, hexoses, hexuronic acids and deoxy-hexoses. The main chain of a hemicellulose could consist of one unit (homopolymer, for instance xylans) or alternatively, it could have two or more units (heteropolymer) like glucomannans (Figure 2). These units are usually side groups of a main chain (backbone), like 4-*O*-methylglucuronic acid, with galactose as the side chain to the backbone [6, 7]. There is a considerable difference in the structure and composition of the hemicelluloses found in both hard and softwood. Additionally, the content and composition of hemicelluloses present in the wood stem, branches, roots and back are also different.

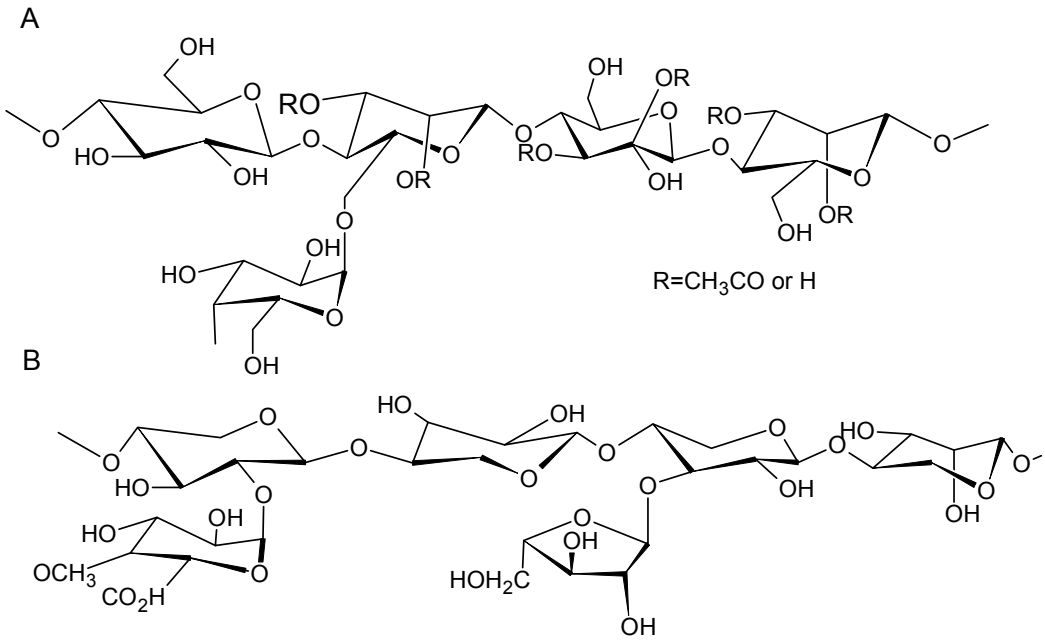


Figure 2. A) glucomannans and B) xylan are the most common units in soft and hardwood, respectively (adapted from ref. [12])

1.1.4. Lignin

Lignin is the second most abundant and important polymeric organic substance in the plant world after cellulose. Lignin provides an increase in the mechanical strength properties of the tree. The amount of lignin present in different plants is quite variable and, for instance, in wood species it ranges from 20 to 40 wt-%, whereas aquatic and herbaceous angiosperms as well as many monocotyledons (horse tail species) have less lignin compared to various wood species. [6, 7, 11]. Lignin is generally described as a three dimensional, amorphous polymer that glues the fibres together in the middle lamellae and the fibrils together in the cell wall. Lignin can be determined quantitatively (albeit with difficulties) after removal of extractives followed by degradation and removal of cellulose and hemicelluloses with strong acids [6, 7, 11]. Lignin's polymers are made up of phenylpropane units and its building blocks are phenols that are linked together in a three dimensional structure. The phenylpropane units are p-coumaryl alcohol, coniferyl alcohol and

sinapyl alcohol, respectively (Fig 3). A schematic picture of a possible fragment of lignin is shown in figure 4.

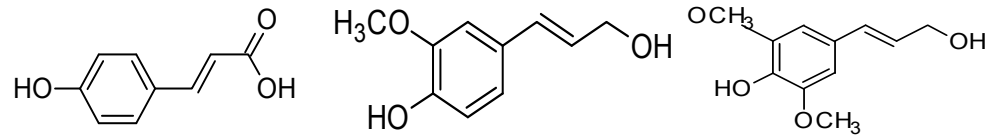


Figure 3. The building blocks of lignin (adapted from refs. [7, 11])

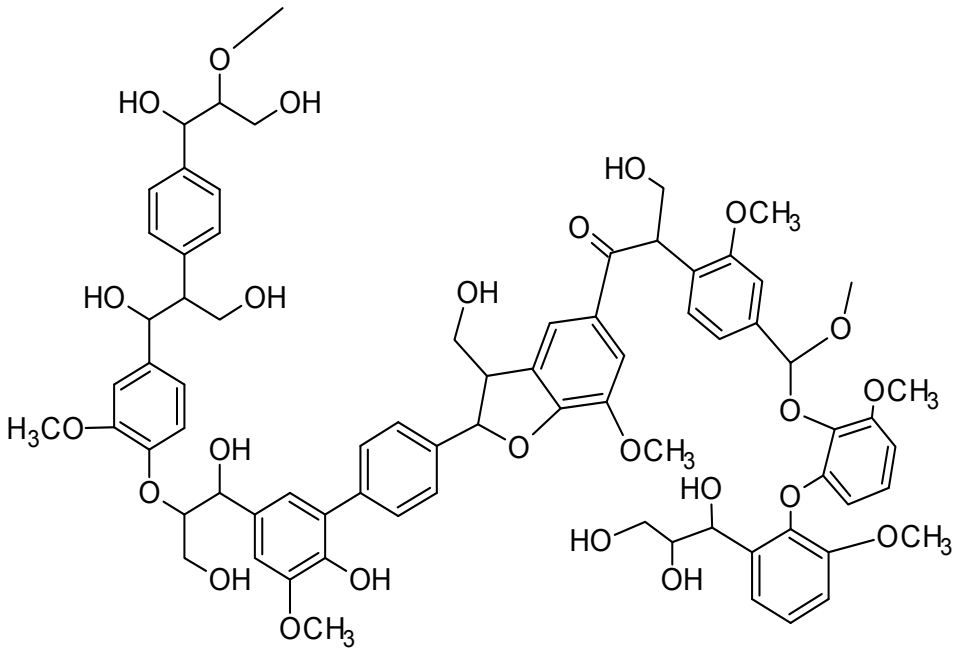


Figure 4. A possible fragment of a lignin co-polymer based on these three monomers (adapted from refs. [12]).

1.1.5. Extractives

The term wood extractive covers a large group of heterogeneous compounds and most of them are low-molecular substances that can be extracted from wood by means of polar and non-polar solvents. Unlike lignin, cellulose and hemicelluloses, extractives do not give any mechanical support to the tree. Some extractives take part in the catalytic

biosynthetic processes and are energy sources for the wood cells. In addition, extractives can also protect the wood against microbiological damage or insect attack. The protection extractives provide to the tree can be physical (resin is tacky) or chemical (many extractives are toxic to bacteria, fungi and insects) [7, 11]. Wood extractives can be classified into two groups according to the kind of solvents which can be used for their extraction. Lipophilic extractives such as resins, fats, and waxes can be extracted with non-polar solvents such as hexane, dichloromethane etc. Hydrophilic extractives for example phenols, sugars and inorganic salts, are extracted with polar solvents such as acetone, water and ethanol [7, 11].

1.2. Fractionation methods

All components of lignocellulosic materials can be utilized for the production of biofuels and chemicals. Fractionation of wood into its different constituents facilitates the utilization of each fraction, for instance, cellulose can be e.g. hydrolyzed to glucose using acids or enzymes. Further, the obtained monosaccharides and can also be transformed into various valuable chemicals. There are several methods developed over the years for the fractionation lignocelluloses and hydrothermal and other methods like steam explosion, carbon dioxide explosion and also hot water treatment have been introduced. Chemical treatment can also be facilitated and include those of dilute acid treatment [13], alkali treatment, organosolv process using organic solvents, ammonia fibre explosion (AFEX), ammonia recycle percolation and ozonolysis [14, 15].

1.3. Physicochemical processes

1.3.1. Mechanical comminution

Comminution of lignocellulosic materials through a combination of chipping and grinding can be applied to reduce cellulose crystallinity. The size of the materials is usually between 10-30 mm after chipping and 0.2-2 mm after milling. Milling has been found to be a very effective in breaking down the crystallinity of the cellulose and improve the digestibility of the biomass [16, 17]. Nevertheless, the process is very energy intensive and its profitability is typically sensitive to the fluctuations in (electrical) energy price.

1.3.2. Steam explosion

Steam explosion is a pre-treatment process used for lignocellulosic material which involves treating of the chipped lignocellulosic material with high-pressurized saturated steam and, after attaining a desired reaction time, the pressure is swiftly reduced. The water inside the material vaporizes and expands rapidly by disintegrating the material. This rapid change in pressure causes the material to undergo an explosive decompression. Furthermore, a great reduction in the particle size is obtained and at the same time the porosity of the material increases. Steam explosion is typically initiated at temperature and pressure ranges of 160-260°C and 0.69-4.82 MPa, respectively, for a few seconds [17] before the material is exposed to atmospheric pressure. The effect of steam explosion on the lignocellulosic material is mainly the transformation of the lignin owing to high temperatures. Additionally, steam explosion causes degradation of hemicelluloses, thus increasing the potential of cellulose hydrolysis. Several factors affect the steam explosion process, such as residence time, temperature, moisture content and particle size. Steam explosion pre-treatment is a more advantageous process compared to the mechanical comminution process because it requires lower energy input and lower recycling and environmental cost compared to the mechanical comminution process. The limitations of the steam explosion as a pre-treatment process include destruction of a portion of the xylan fraction although the lignin-carbohydrate matrix is not, however, totally disrupted, and compounds that may inhibit micro-organisms used in downstream process are generated. There will be formation of degradation products that are inhibitory to microbial growth, enzymatic hydrolysis, and fermentation. Because of the formation of such inhibitory compounds for microbial growth, enzymatic hydrolysis and fermentation, the pre-treated lignocellulosic material should be washed with water, thus leading to a reduction of the overall saccharification yield through the removal of water soluble sugars [16-18].

1.3.3. Ammonia fiber explosion (AFEX)

Ammonia fiber explosion is another physicochemical pre-treatment process in which lignocellulosic materials are treated with an aqueous ammonia solution, at moderate temperatures (60-100°C) and under a pressure of ~5 MPa for a period of time, followed by a rapid pressure decrease. This process is similar to the steam explosion process and a

typical ammonia dosage is 1-2 kg ammonia/kg dry biomass and, at 90°C, a residence time of 30 min is applied. AFEX pre-treatment process can improve the fermentation rate of various crops. During AFEX pre-treatment a small portion of the solid material is solubilised, in other words, no hemicellulose or lignin is lost [16, 17, 19]. Hemicellulose is degraded to oligomeric and deacetylated sugars which could be the reason for the fact that hemicelluloses are solubilized. The structure of the material changes due to increased water holding capacity and higher digestibility. Over 90% hydrolysis of cellulose and hemicellulose has been obtained after AFEX pre-treatment of lignocellulosic material with a low lignin content [16, 17]. The AFEX pre-treatment process is not, however, very efficient for lignocellulosic material with high lignin content. Furthermore, the cost of the recovery of spent ammonia makes AFEX an expensive pre-treatment method [16-18, 20].

1.3.4. Carbon dioxide explosion

As an attempt to develop improvements to the previously described pre-treatment methods of lignocellulosic materials (steam explosion and AFEX), new methods are sought after that would require lower temperatures compared to temperature needed for steam explosion, and also would be less expensive compared to the ammonia explosion. The idea of using supercritical carbon dioxide explosion was suggested as an alternative approach [21]. Carbon dioxide molecules could be comparable in size to ammonia and water molecules and they would penetrate into small pores that are accessible to ammonia and water molecule. Moreover, carbon dioxide forms carbonic acid during water dissolution. Generally, carbonic acid should increase the hydrolysis rate of hemicelluloses and cellulose. At low temperatures, decomposition of the monosaccharides by the acid is limited, whereas during an explosive release of the carbon dioxide pressure, the structure of the lignocellulosic material is disrupted and thus, an increased accessibility to the substrate occurs leading to efficient hydrolysis [16, 21]. No degradation of sugar occurs during the carbon dioxide explosion pre-treatment because the process is carried out at lower temperatures compared to steam explosion. Furthermore, the of inhibitory compounds are not formed as in steam explosion [21].

1.4. Chemical processes

1.4.1. Acid hydrolysis

Lignocellulosic materials have been treated using concentrated acids such as H_2SO_4 and HCl, and quite encouraging results have been achieved using acid hydrolysis to release fermentable sugars [22]. Although concentrated acids are powerful agents for cellulose hydrolysis, these are, however, toxic, corrosive and hazardous. Furthermore, corrosion resistant reactors are required, thus making this an expensive process. Dilute acids such as H_2SO_4 have been reported to have efficiently hydrolysed hemicelluloses to xylose and other sugars as well as to further facilitate a transformation of xylose to furfural [16, 17]. There are basically two types of dilute acid pre-treatment processes, namely; high temperature (higher than 160° C), continuous-flow process for low solid loading (5-10%: weight of substrate /weight of reaction mixture) and low temperature (less than 160° C), batch process for high solid loading (10-40% weight of substrate /weight of reaction mixture) [17]. Also this process suffers from issues like high cost and need of neutralization (reduced pH) for the downstream enzymatic hydrolysis or fermentation processes are required [16, 17].

1.4.2. Ionic liquids

Ionic liquids (ILs) have been widely studied as fractionation solvents for lignocellulosic materials [5, 22-25] since they can potentially provide a more environmentally friendly platform compared to previously mentioned processes. Room temperature ILs are molten salts usually made up of organic cations coupled to inorganic or organic anions and their melting points are generally below the boiling point of water (100°C). ILs have tunable properties making them suitable as solvents for many applications [26]. In spite of the great solvation advantage of ILs and their tunable properties, many ILs are rather expensive and, thus, often render them less cost efficient as an industrial scale solvent for dissolution of lignocellulosic materials. Likewise, in most of the publications involving ILs as fractionation solvents for lignocellulosic materials, the treatment procedures require extensive drying of the material, since 'classical' ILs are sensitive to moisture (loss of solvent power) and, in addition, a milling step (physical treatment) of the material

into smaller particles is typically required. Naturally, these steps further add to the processing cost [5, 23, 25, 27, 28].

1.4.3. Switchable ionic liquids

Switchable ionic Liquids (SILs) have been studied as fractionation solvents for lignocellulosic materials [29, 30]. SILs are solvents capable of ionic/non-ionic switching by addition or removal of one compound, a trigger which is usually an acid gas [31-33]. In addition, SILs can be prepared from inexpensive chemicals such as monoethanol amine (MEA), glycerol; an amidine/guadinine or other organic superbases (e.g. 1,8-diazabicyclo-[5.4.0]-undec-7-ene, DBU). A typical trigger can be obtained from industrial flue gases like, for example, CO_2 or SO_2. In an industrial scale SILs could, in fact, be synthesised in-situ and/or on-site, since the acid gases are present in the industrial sites.

1.5. Aim and scope of the research

The aim of this study was to synthesize novel switchable ionic liquids formulated from affordable, abundant and, preferably, environmentally friendly building blocks. Trials with various superbase classes such as amidines, e.g. 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU), 1,5-Diazabicyclo[4.3.0]non-5-ene (DBN) and guanidines, e.g. 1,1,3,3-tetramethylguanidine (TMG) were conducted. The use of benign, non-toxic hydroxyl group containing compounds like e.g. glycerol, (obtained as e.g. a by-product in biodiesel production) monoethanolamine (MEA), choline chloride, as well as alcohols and alcohol sugars can be realized, in addition to various acid gases, like CO_2, SO_2. The synthesis and characterization of one sample new SIL has been reported in article **[I]**. Subsequently, to test the synthesized SILs as fractionation solvents for lignocellulosic biomass, series of tests were performed to pinpoint the optimal reaction parameters for the fractionation process.

2. EXPERIMENTAL

2.1. Chemicals

Organic superbases, as example, 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU) (99 %) 1,5-Diazabicyclo[4.3.0]non-5-ene (DBN) (99 %), 1,1,3,3-tetramethylguanidine (TMG) (99 %), monoethanol amine (99 %) and glycerol (99+ %) were used as received from Sigma Aldrich. Supercritical grade CO_2 (99.999%, H_2O < 0.5 ppm) and SO_2 (99.998%, H_2O < 3 ppm) were provided by AGA Oy. Solvents used as anti-solvents were as follows; acetone (J.T. Baker, 99.5%), ethanol (Altia, 99.5%), methanol (Merck, 99%), isopropyl alcohol (IPA) (Merck, 99%) and de-ionized water (Millipore).

2.2. Preparation and characterization of switchable ionic liquids (SILs) [I]

SILs are solvents capable of ionic/non-ionic transformation, due the addition or removal of a stimulus. This stimulant or trigger is usually an acid gas bubbled into the mixture. These new types of solvents can be synthesized by mixing a superbase such as an amidine, e.g. 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU), 1,5-Diazabicyclo[4.3.0]non-5-ene (DBN), or a guanidine, e.g. 1,1,3,3-tetramethylguanidine (TMG), with another molecule containing hydroxyl groups. Representative examples are biodegradable compounds like e.g. glycerol or ethanol. The molar ratio of amidine/guanidine to hydroxyl containing compound is calculated based on the number of hydroxyl groups in the alcohol or alkanol. The acids gas or mixtures of acid gases is then bubbled through the liquid mixture under rigorous stirring. The ionic liquid is formed in an exothermic reaction when the mixture reaches equilibrium; the formed SILs can be reversed back to the starting mixtures of the superbase and hydroxyl containing compound by purging out the acid gas with an inert gas such as nitrogen or argon or, increasing the temperature of the sample above the thermal decomposition temperature of the respective SIL. The reverse can be made faster by increasing the ‘back-switching’ temperature. Thus, in this study, a number of straightforward, easy-to-carry out recipes following the guidelines for the synthesis of SILs are described.

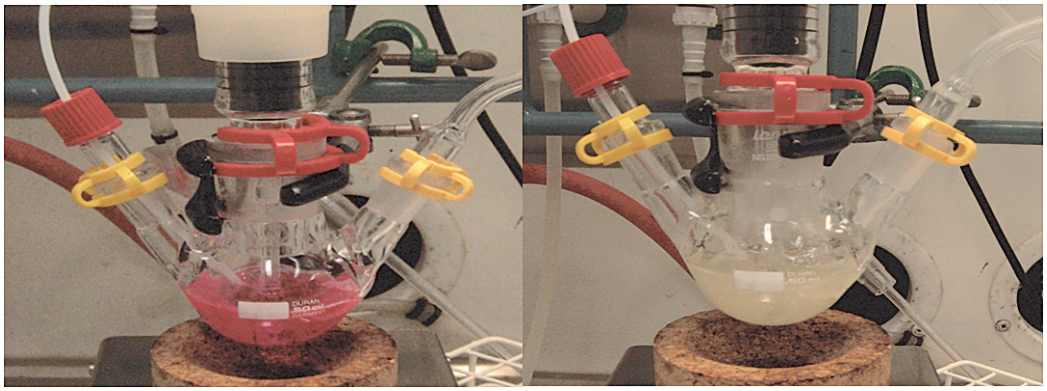


Figure 5. The solvent before and after switching demonstrated by the colour change from red to milky.

The synthesized SILs were characterized by various methods. The viscosities of the solvents were measured by using a VOR Bohlin Rheometer at 25°C. The low viscosity samples were measured with the bob/cup geometry and the high viscosity samples with the cone/plate geometry. The viscosity was calculated by taking the average of ten experimental points (1 point every 30 seconds) at a constant shear rate of 11.6 per second. The viscosity measurements were carried out for selected SILs before and after switching using a Bohlin VOR rheometer.

The decomposition temperature was determined by Thermo-Gravimetric Analysis (TGA) whereas Differential Scanning Calorimetry (DSC) was applied for the determination of melting and glass transition points of the SILs.

The SILs were also characterized by Fourier Transform Infrared Spectroscopy (FTIR-ATR) spectroscopy, with a Bruker IFS66/S FTIR spectrometer equipped with a mercury-cadmium-telluride (MCT) detector. A small sized cell made from Teflon® was used in the spectroscopic measurements. The experimental setup for the FTIR-ATR technique has been described elsewhere in ref. [34] and paper **[I]**.

Furthermore, the synthesized switchable ionic liquid (SIL) was characterized by means of Nuclear Magnetic Resonance Spectroscopy (NMR) in a Bruker AV 600 to confirm the presence of carbonate salts. ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR spectra of the formed SILs were recorded neat at 60°C.

Miscibility tests were conducted using a host of organic solvent to determine the SIL solubility. The change in polarity was viewed by addition of a solvatochromic dye.

The moisture content was analysed by Karl-Fisher titration and carried out by diluting ~50-80 mg of the SIL in "dry" methanol. The titrant used was HYDRANAL composite 5K. Calibrations were performed by first checking the consumption of Composite 5K when only methanol was titrated. Then one droplet of water (20-30 mg) was added to 5 ml methanol and the consumption was checked. The factor mg H_2O/ml Composite 5K was close to the value reported on the bottle which was between 5.2 and 5.

2.3. Lignocellulose analysis

2.3.1. Carbohydrate analysis

The carbohydrate content of the samples was analyzed by Gas Chromatography (GC) after acid methanolysis or acid hydrolysis of the sample. Before GC analysis silylation was performed. The purpose was to determine the hemicellulose and cellulose content of each and every sample, respectively [35, 36]. For GC analysis, about 2 µl of the silylated sample was injected through a split injector (260°C, split ratio 1:5) into a capillary column coated with dimethyl polysiloxane (HP-1, Hewlett Packard). The column length, internal diameter and film thickness were 30 m, 320 µm and 0.17 µm, respectively. The following temperature program was applied: 4°C/min from100 – 175°C followed by 12°C/min from 175 – 290°C. The detector (FID) temperature was 290°C. Hydrogen was used as a carrier gas. The different peaks were identified by Mass Spectrometry (GC-MS).

2.3.2. Lignin content determination

The lignin content was determined using a modified Klason lignin method in which the boiling for 4 hours to complete hydrolysis of the polysaccharides was replaced with an autoclave treatment at 125°C and 20.3 Psi for 90 min [37, 38].

2.3.3. FTIR spectroscopy

The FTIR spectra of the treated and untreated lignocellulosic samples were recorded using a Bruker infrared fiber sensors (IFS), (Bruker optical GmbH, Germany) 66/S. The

Fourier Transform Infrared (FTIR) Spectrometer was equipped with an attenuated total reflectance (ATR) cell and with a DTGS detector. The KBr disc method for solids (300 mg KBr contained 1% finely ground samples) was applied. Spectra were recorded at the range between 4000 and 500 cm^{-1}, 64 scans were collected with a resolution of 4 cm^{-1}.

2.3.4. NMR spectroscopy

The ^{13}C CP/MAS NMR spectra were acquired on a 500 MHz Bruker Avance III spectrometer (Bruker Biospin, Germany) equipped with a 4 mm MAS probe. 50% deionized water was added before analysis. 1 ms contact time was used and 4096 scans were collected for each sample. A Gaussian window function was used in the spectral processing performed in Topspin 3.1 (Bruker Biospin, Germany). Samples were analyzed at ambient temperature.

2.3.5. Gel permeation chromatography

Gel permeation chromatography (GPC) analysis of the undissolved treated and untreated wood chips for both hard-and softwood were performed. In order to remove the (residual) lignin the following acid chlorite delignification conditions described in paper **[V]** was applied. In addition, ethylenediamine (EDA) pre-treament of the delignified holocelluloses was carried out with following the method described in ref. [39] and can also be found in paper **[V]**.

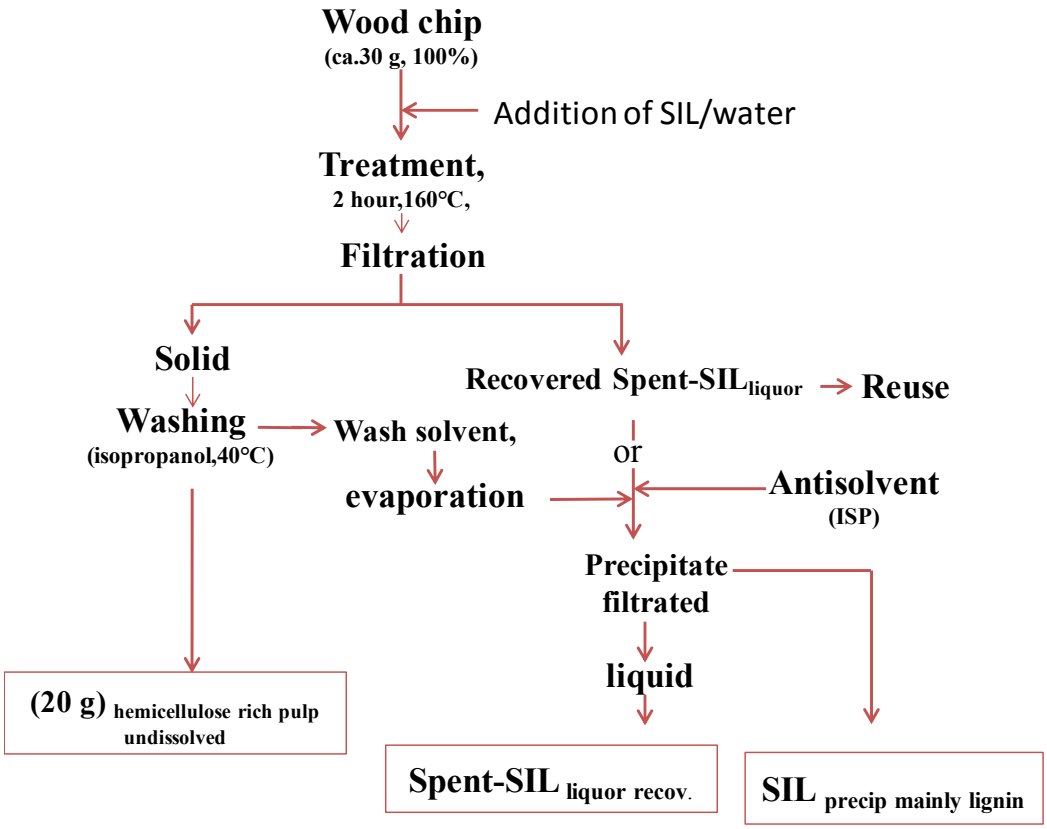
2.3.6. SEM images

The Scanning Electron Microscopy (SEM) images were taken using a Leo Gemini 1530 Scanning Electron Microscope equipped with a ThermoNORAN Vantage X-ray detector for EDXA analysis. SEB Electron detector voltage was at 15 kV, whereas the ILSE detector worked at 2.70 kV.

2.3.7. X-Ray diffraction

Untreated and SIL treated wood chip samples were analyzed by powder X–ray diffraction (XRD) using a PANalytical X´Pert PRO alpha 1 diffractometer equipped with primary beam Johansson monochromator to generate pure Cu $K_{\alpha 1}$ radiation (1.5406 Å; 45kV, 30 mA). Samples were prepared into steel-made sample holder with 16 mm radius sample cavity. X´Celerator detector in a continuous scanning mode was used to collect the data

in 2θ range of 3–71° with a step size of 0.017° and counting time of 200 s per step (overall time of ~ 2 h). A programmable divergence slit (PDS) was used in automatic mode to set the irradiated length on sample to 10 mm together with a fixed 15 mm incident beam mask. Soller slits of 0.02° rad were used on both incident and diffracted beam sides. The more detailed descriptions and working methods can be found in paper **[VII].**



Scheme 1. STHT approach for fractionation of wood using a SIL as a solvent.

2.4. Selective extraction of hemicelluloses from spruce flour using SILs [III]

Dissolution of wood using conventional ionic liquids has, as one of its bottle necks the high viscosity of the solution after dissolution. This has consequences in term of recycling, recovery and reuse of an ionic liquid rendering it a less viable solvent for biomass. The dissolution of lignocellulosic material using new switchable ionic liquids (SILs) was investigated herein to see if their ability to be 'switched' can facilitate an easy

solvent recycling and recovery of dissolved components. SILs used for this test were synthesised from the mixture of an amidine (1,8-diazabicyclo- [5.4.0]-undec-7-ene (DBU)) with alcohol (1-hexanol or butanol) and gaseous CO_2 as trigger. SILs were then used to treat wood meal (~ 40 mesh) at 60°C for 5 days with and without stirring.

2.5. Treatment of birch wood by a switchable ionic liquid based on DBU-glycerol carbonate [IV]

It was demonstrated that SILs are potential novel solvents for the fractionation of lignocellulosic material into suitable fractions. However, the fractionation efficiency was not comparable to those obtained with conventional ILs, mainly due to the low treatment temperature. Therefore, the fractionation of lignocellulosic material (birch, *Betula pendula.*) was investigated using new types of SILs. These were based on glycerol, CO_2, and an amidine (DBU). The new SIL has one major advantage compared to earlier SILs presented, since its decomposition temperature is significantly higher. This allows for higher treatment temperatures (and consequently, more efficient fractionation). Wood was fractionated without any mechanical agitation, under normal pressure and at 100°C. The process of the dissolution was followed for five days. In view of a possible industrial application, the reuse possibility of the spent SILs and the recovery of the dissolved material from the spent SILs were also studied.

2.6. DBU-MEA-SIL as a delignification solvent for birch (*Betula Pendula*): switching with CO_2 vs. SO_2 [V]

As a new alternative, different types of SILs were studied as fractionation solvents for lignocellulosic materials. Furthermore, the use of SILs as solvents for lignocellulosic material can facilitate selective extraction or selective enrichment of the material by the choice of the trigger (CO_2 or SO_2) alkanol amine or amidine constituting the SILs. Characteristically, lignin removal from lignocellulosic material can be expedited by means of a range of industrial processes, commonly applied in pulping of wood chips and other fibers. An example of such industrial process is the Kraft process operating at ~170° [7]. There are mainly two structural changes occur to lignin during chemical pulping, which has been discussed in refs. [23, 40, 41]. However, most existing processes used in the fractionation and separation of lignin from lignocellulosic material are capital

intensive due to use of high pressure, elevated treatment temperatures, or the need of special materials upon processing equipment due to the use of acids and bases at high temperature [23, 24]. Herein fractionation of birch wood chips was demonstrated using SILs based on monoethanol amine (MEA), an amidine, (DBU) and triggers, such as CO_2 and SO_2. Birch meal ~1 mm was treated with SIL applying a SIL-to-wood ratio of 5:1 by weight, and the treatment temperature was 120°C for 24 h under normal pressure and under constant stirring. The goal was to mainly obtain selective fractionation of one or two of the main components of the wood. Selective extraction of lignin from the lignocellulosic material using SILs seems to be the most desirable option, since these SILs can be produced in-situ. Also, working under notoriously dry conditions (as is common for 'classical' ionic liquids) is not needed and the process is thus easy to handle.

2.6.1. An optimal fractionation approach using an alkanol amine -superbase switchable ionic liquid as a solvent [VI]

The use of SILs as solvents for lignocellulosic material can facilitate selective extraction or selective enrichment of the material by the choice of the trigger (CO_2 or SO_2) together with alkanol amine or amidine constituting the SIL. In earlier cases the treatment time was unnecessary long, and shorter treatment times would constitute a more cost effective process in an industrial scale. Furthermore, the use of large amounts of SILs and drying of the wood would also add to the process cost. Thus, an addition of water to the wood-SIL mixture or the use fresh non-dried wood was attempted, since it was observed that water does not significantly influence the wood dissolution efficiency of the SIL [30, 42, 43]. Consequently, this can be seen as an approach to reduce the SIL consumption and as an adaptation to industrially feasible operational conditions. The search to optimize conditions for selective fractionation of woody biomass into its various fractions was continued by using an alkanol amine (MEA) and an organic superbase (DBU) derived SIL. The STHT approach involves the pathway according to Scheme 1 to fractionate wood into cellulose, hemicellulose and lignin, using SIL as a solvent. Wood (approx. 30 g) was immersed in the SIL (approx. 150 g) and 90 g water was added to obtain a 1:3:5 weight ratio mixtures. The aqueous SIL-wood mixture was kept at 160°C under normal atmospheric pressure for two hours without stirring. While the mixture was still hot, the undissolved wood fraction was separated using vacuum filtration. The undissolved wood

material was washed several times with isopropyl alcohol at about 40°C until no visual evidence of any traces of the SILs remaining on the undissolved fraction could be seen.

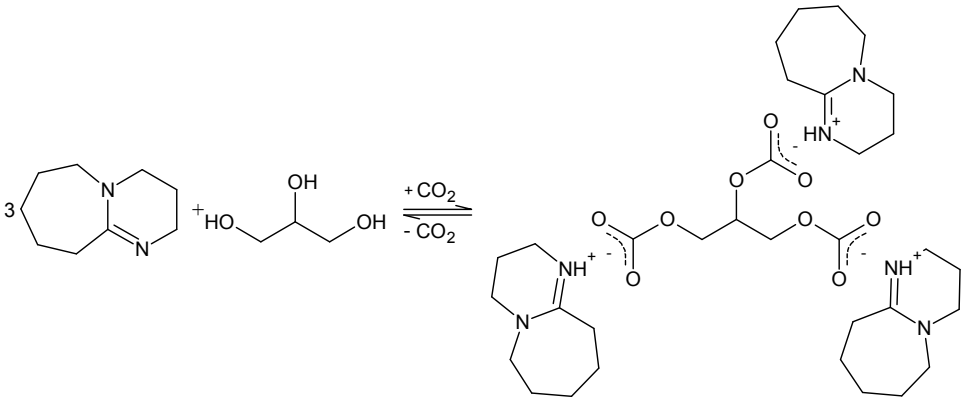
2.7. The composition and crystallinity of birch chips (*Betula Pendula*) upon 'DBU-DEA-CO_2 SIL' alkanol amine–organic superbase-derived SIL treatment [VII]

In essence, SILs were used as alternative solvents for fractionation of lignocellulosic materials – one motivation being that they offer a platform associated with milder treatment conditions and, consequently, giving possibility to hamper product degradation. The aim of this study was to fractionate birch wood using a SIL based on diethanol amine (DEA), an amidine, 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU), and CO_2. The processing was carried out at mild treatment conditions in order not to degrade the cellulose or to destroy any other lignocellulosic components. In addition, the changes in crystallinity of the wood components occurring during SIL treatment were investigated. The treatment of birch chips using similar SILs was already studied. In this study, however, a two-step SIL treatment was applied in order to obtain a fraction more enriched in cellulose.

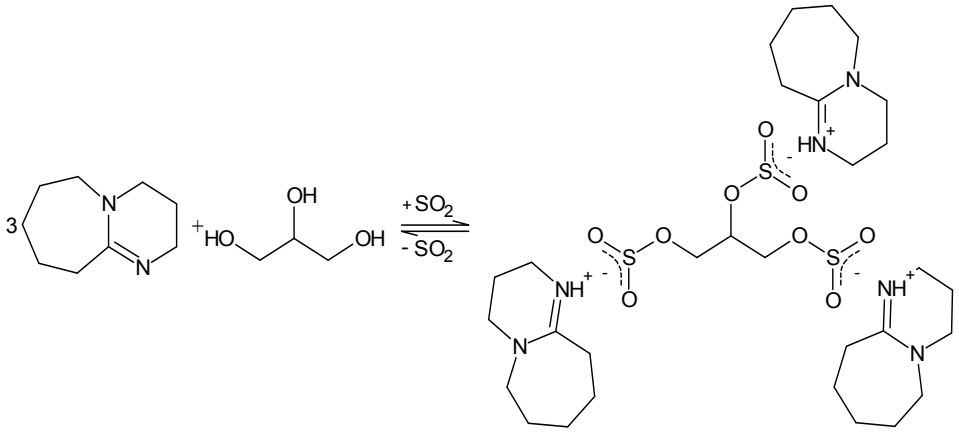
3. RESULTS AND DISCUSSION

3.1. Synthesis of DBU-glycerol-CO_2-SILs and DBU-glycerol-SO_2

Generally, the SILs were synthesized by means of bubbling CO_2 or SO_2 through the liquid mixture. Also, the ratio of amidine/guanidine to hydroxyl containing compound was calculated based on the number of hydroxyl groups present in the alcohol or alkanol. DBU-glycerol-SILs were prepared by passing either CO_2 or SO_2 through the mixture containing 3:1 molar amounts of DBU and glycerol. The weight increase with the carbonate SIL corresponded to the molar ratio of 3.14:1 (DBU to CO_2), whereas for the glycerol sulfonate SILs, molar ratios of 3:3.8 and 3:1 (DBU to SO_2 and DBU to glycerol) were achieved, respectively. These results indicate that all OH-groups of the glycerol in the SO_2 version reacted upon formation of the ionic liquids according to Schemes 2 and 3. This observation was also supported by NMR and FTIR studies conducted, paper **[I]**.



Scheme 2 Proposed reaction scheme for the formation of DBU-glycerol-CO_2-SIL



Scheme 3 Proposed reaction scheme for the formation of DBU-glycerol-SO_2-SIL

3.1.1. Characterization of the DBU/Glycerol/CO_2 system by ^{1}H and ^{13}C NMR spectroscopy

NMR spectra were measured on neat samples of DBU and glycerol (3:1), before and after the addition of CO_2. Due to the high viscosity of the SILs at room temperature, the NMR spectra were recorded at 60°C to minimize signal broadening. ^{1}H as well as quantitative ^{13}C NMR spectra were recorded. In order to assign the signals and to confirm the structures, different 2D NMR techniques were also utilized. The spectra of the samples are shown in Figs. 6 and 7, respectively.

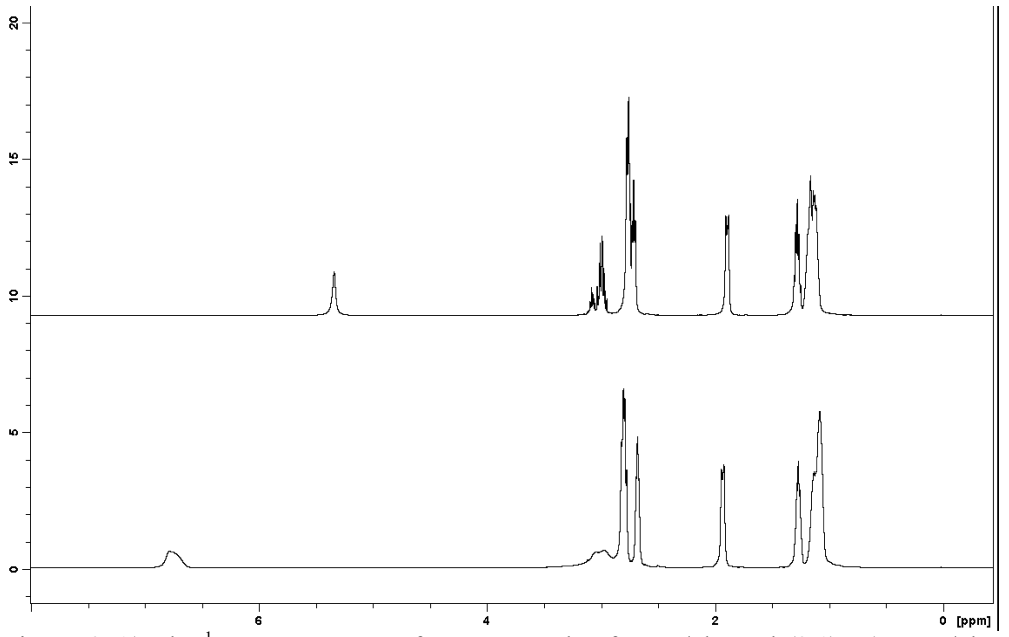


Figure 6. A) The ^{1}H NMR spectra of a neat sample of DBU/glycerol (3:1), B) DBU/glycerol (3:1)/CO_2 recorded at 60°C using external DMSO-d6 as a reference

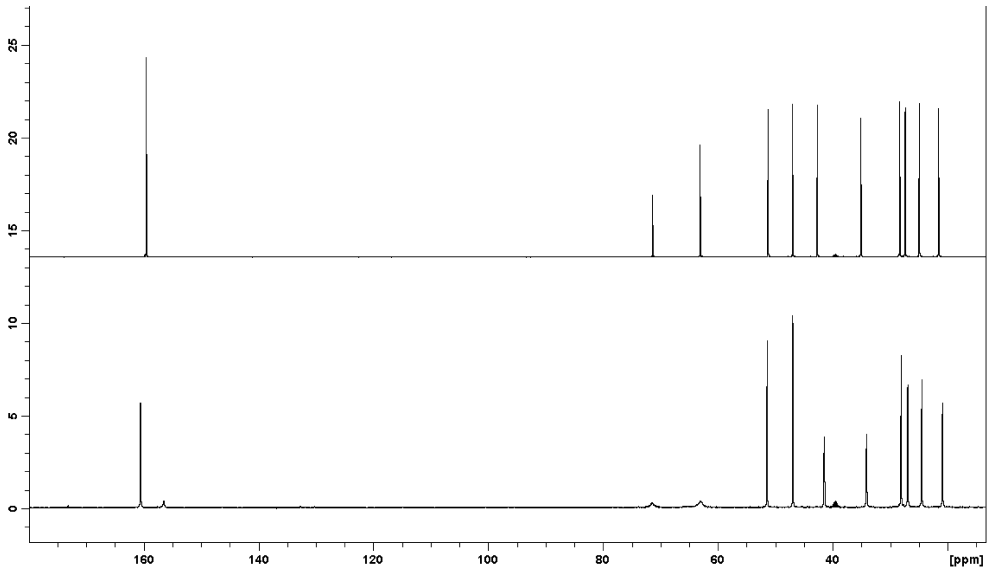
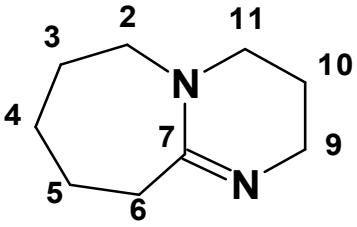


Figure 7. A) The ^{13}C NMR spectra of a neat sample of DBU/glycerol (3:1) B) DBU/glycerol (3:1)/CO_2 recorded at 60°C using external DMSO-d6 as a chemical shift reference.

The ^{1}H NMR spectral data is shown in paper **[I]** and the ^{13}C NMR spectral data are also shown in paper **[I].** Most of the signals in the ^{1}H NMR spectra were broad, complex and

a detailed spectral analysis was not performed. However, the assignments of ^{1}H and ^{13}C NMR signals were performed using standard 2D correlation NMR spectroscopy. The atoms of DBU are numbered according to the Scheme 4



Scheme 4. Numbering of the carbon atoms in DBU

SIL formation resulted in small signal shifts in the ^{1}H NMR spectrum, and CO_2 addition resulted in broadening of the signals. This was most marked in the signals of the protons of glycerol and the acidic proton of the protonated DBU. Moreover, the signal of the latter was shifted downfield by ca. 1.4 ppm, indicating an increase in acidity. The formation of a carbonate was confirmed by performing an additional experiment with a glycerol-DBU ratio of 2:1. The ^{1}H NMR and ^{13}C NMR spectra now showed signals which were then assigned to non-derivatised glycerol as well as signals probably derived from the glyceryl carbonate. The intensity of the ^{13}C NMR signal previously assigned to the carbonate carbon also increased. The presence of glycerol carbonate was shown by long-range $^{1}H/^{13}C$ correlation spectroscopy (HMBC). In this spectrum (Fig.8), connectivity was observed between the H-1 proton in glycerol and the carbonate carbon as shown by the presence of a correlation signal situated at 3.18/157.34 (H/C) ppm. The other crosspeaks seen in Fig.8 are connectivities between the ring hydrogens and the bridgehead carbon in DBU.

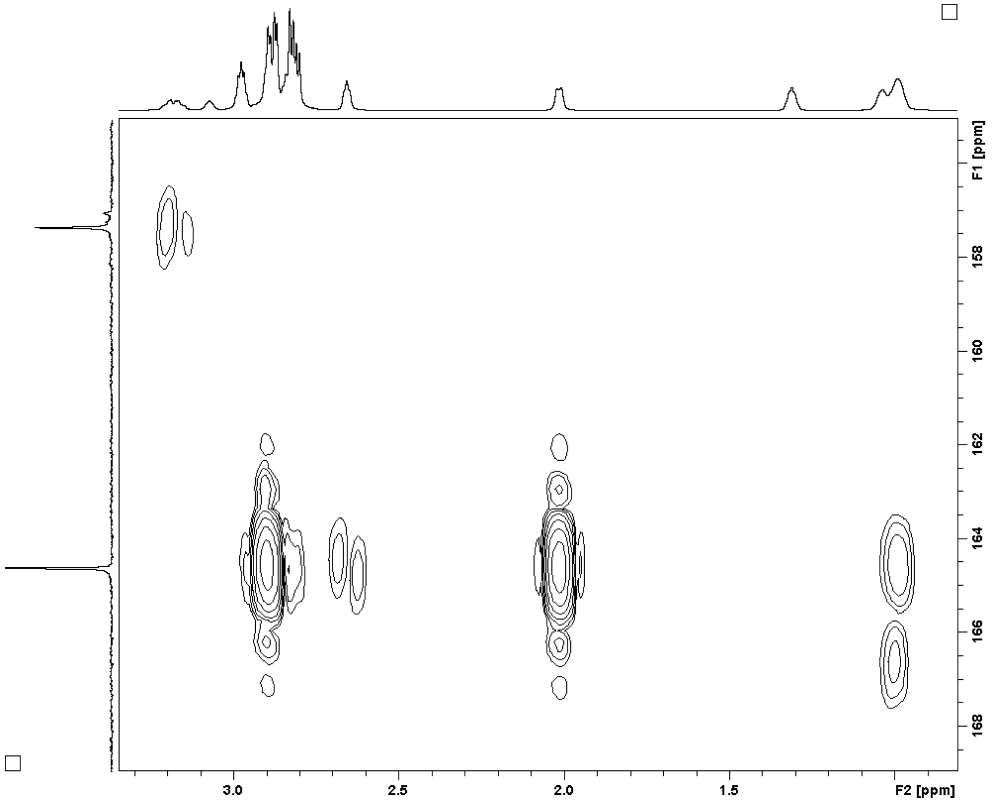
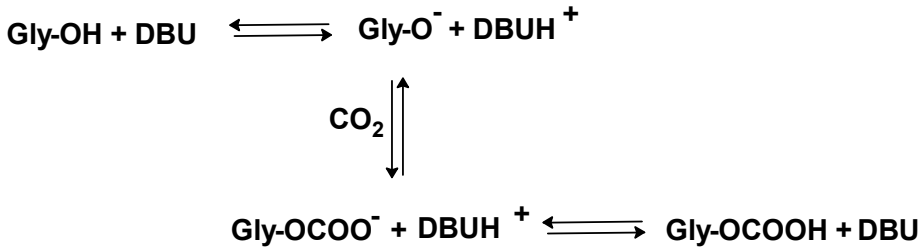


Figure 8. The partial HMBC 2D NMR spectrum of DBU/Glycerol (2:1)/ CO_2

Based on the NMR spectral data, the yield of $DBUH^+$ [Gly Carbonate]$^-$ was quite low. The ratio of glycerol-to-CO_2 was around 2:1. The results also indicated that most of the carbonate formed was a monocarbonate at C-1 of glycerol. Upon addition of CO_2, a complex mixture of equilibria was formed, in which the main reactions was protonation of DBU and the formation of glyceryl monocarbonate. This resulted in a mixture of two salts, [DBUH][Gly-O] and [DBUH][Gly-OCO2], respectively (Scheme 5). Moreover, the mixture may contain small amounts of carbonate formed by reaction at C-2 of glycerol in addition to bi- and tricarbonates.



Scheme 5. Proposed reactions for the formation of DBUH+ [Gly- Carbonate]-

3.1.2. FT-IR spectrum of the DBU/glycerol/CO_2 system

The FT-IR spectra in Fig. 9 shows a comparison of the starting materials (a) glycerol and (b) DBU to the product formed after bubbling CO_2 through the DBU/glycerol mixture (c). Protonation of DBU, reduction of the OH vibrations from glycerol, new vibrations from the C-O-C and C=O group and shifts in the C-O vibration should be observed according to Scheme 2. At OH stretching region an IR band at 3286 cm^{-1} could be seen for glycerol whereas the SIL, instead, gave rise to a broad band with a maximum at 3255 cm^{-1}. Consequently, this shift indicates changes due to protonation of DBU and an N-H stretching vibration and was believed together with the unreacted OH-group to give the broad spectral response for the SIL in question at 3000-3600 cm^{-1}(Fig 9c). The bands at 2935 and 2879 cm^{-1} originated from the C-H stretching vibration in the ring and from the alcohol, respectively, and should therefore also be seen even after bubbling of CO_2. In the range of 1600-1300 cm^{-1} bands, DBU gave rise to C=C and C=N ring stretching vibrations. In SILs the band at 1610 cm^{-1} was still strong (from C=N) but the protonation of DBU gives rise to the new band at 1643 cm^{-1}(Fig 9c) [44]. At 1274 and 1050 cm^{-1}, on the other hand, new bands in the SIL spectrum can be observed owing to the asymmetric and symmetric C-O-C stretching vibrations, respectively. C-O stretching vibrations can be seen in Fig. 9 for glycerol at 1030 cm^{-1}. Ketones, aldehydes, carboxylic acids, lactones, amides and alike show a strong C=O stretching absorption band in the region of 1870-1540 cm^{-1} [44-47]. A new band with a low intensity at 1786 cm^{-1} was also observed in the spectrum of the SIL.

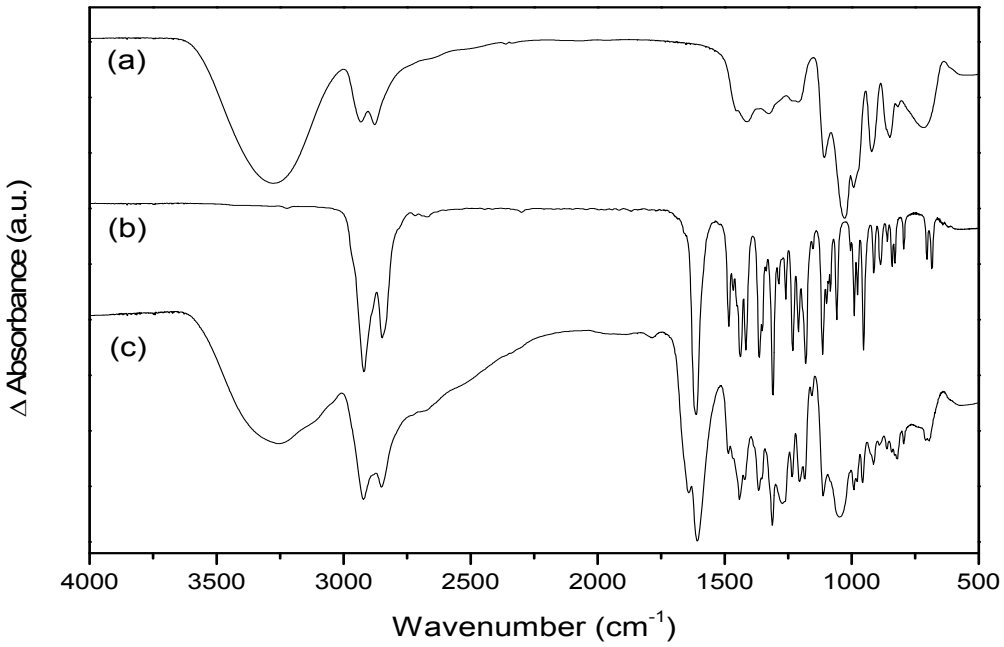


Figure 9. FT-IR spectra of (a) glycerol, (b) DBU and (c) DBU/glycerol after bubbling with CO_2

3.1.3. Physical properties of the SILs

The physical properties of the SILs synthesized from either bubbling CO_2 or SO_2 through a mixture of DBU and glycerol are presented in paper **[I]**. The viscosities of the SILs were much higher than the corresponding, non-ionic precursor mixtures (Table 4). The onset of the decomposition temperature of these switchable ionic liquids were, according to TGA, at ~60 °C for DBU-glycerol-CO_2-SIL and ~120°C for DBU-glycerol-SO_2-SIL, under nitrogen atmosphere, paper **[I]**. However, a shoulder in the weight-loss curves is observed at ~85°C, for the DBU-glycerol-CO_2-SIL. Even a bigger change can be seen at 200°C, for the DBU-glycerol-SO_2-SIL, possibly indicating a change ('collapse') in the nature of the compound. The reason could be that some of the acid gases were liberated to the solution from a deteriorating carbonate/sulfonate structure until that temperature and those were able to loosely maintain the equilibrium in between the released, soluted gas and the carbonate/sulfonate structure. The DBU-glycerol-SO_2-SIL exhibited a higher decomposition temperature compared to the corresponding DBU-glycerol-CO_2-SIL due to the strength of the acid gas binding explained by Heldebrant *et al.* [45]. The strength of the acid gas binding was linearly correlated to the Lewis acidity of the acid gas and, thus

to the decomposition temperature of DBU-glycerol-SO_2-SIL. As mentioned, it was higher compared to the DBU-glycerol-CO_2-SIL [45]. These ionic liquids do not have clear melting/freezing points. However, the DBU-glycerol-SO_2-SIL gave rise to a slightly higher glass transition temperature compared to DBU-glycerol-CO_2-SIL (Fig. 10). According to the Karl-Fischer analysis, both of the SILs contained less than 0.1 wt % of moisture.

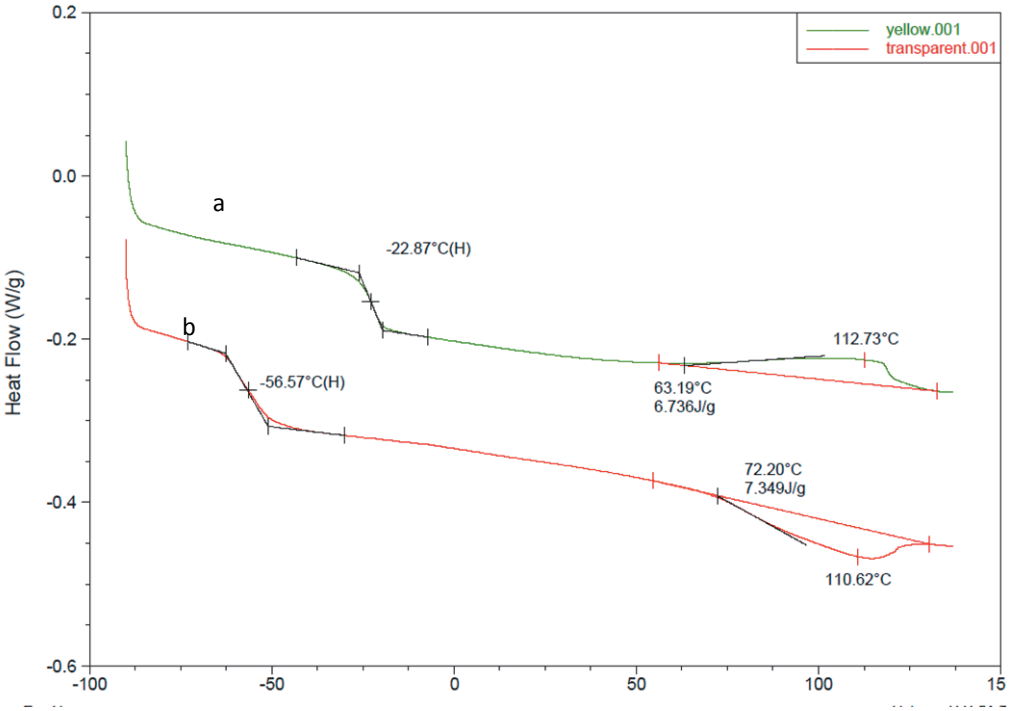


Figure 10. The DSC graphs of (a) DBU-glycerol-SO_2-SIL and (b) DBU-glycerol-CO_2-SIL

The results from miscibility tests with organic solvents are presented in paper **[I]**. The SILs were mainly miscible with polar solvents such as water and methanol. In general, DBU-glycerol-CO_2-SIL is miscible with solvents having dielectric constant over 8 at 25°C. However, this was not the case with acetone, which has the dielectric coefficient of 20.56 at 25°C and is a polar solvent. Instead, some reaction occurred, since white crystals were formed when acetone was mixed with the DBU-glycerol-CO_2-SIL. The same reaction occurred also with tetrahydrofuran. DBU-glycerol-SO_2-SIL was not miscible with hexane and acetone, but was miscible with ethanol and water. To summarize, the

SILs were immiscible with the solvents exhibiting a value of dielectric coefficient below 8, paper **[I]**.

The change in polarity was studied using Nile Red as a solvatochromic dye. The mixture of DBU and glycerol with Nile Red has a red colour which is common for low polarity solvents (Fig. 5a). However, when CO_2 was bubbled through the mixture, the color changed from red to milky as the polarity of the liquid increased, as illustrated in Fig. 5b. The colour change occurred to the other direction when nitrogen was bubbled through the liquid. It can be concluded that CO_2 can be used as a trigger for switching the DBU-glycerol mixture from molecular to ionic form and N_2 for switching the ionic form back to the molecular mixture.

3.2. Selective extraction of hemicelluloses from spruce flour using SILs [III]

3.2.1. The composition of wood chips before dissolution

The composition of the native Spruce wood (*Picea abies*) and its water content are presented in Table 1. The amounts of the three major components in wood, namely cellulose, hemicelluloses and lignin are consistent with the ones presented in refs [7, 11, 35].

Table 1. The results from the analysis of spruce before treatment with SILs

Wood sample	mg/g dry mass
extractives	13
lignin	270
hemicelluloses	260
cellulose	450
inorganics (ash forming matter)	7

3.2.2. Influence of wood extractives on wood dissolution

The presence of wood extractives on the dissolution of wood was also studied for the following wood samples: 1) wood samples which have been pre-extracted using the Soxhlet method, and 2) dried native wood. The dissolution results are presented in Figs. 11 and 12 as well as Table 2. The DBU-butanol-CO_2-SIL exhibited higher dissolution efficiency with about 36 wt-% reduction of the total amount of hemicelluloses in the

wood compared to the DBU-hexanol-CO_2-SIL and 14 wt-%, reduction for the native spruce wood. Furthermore, the pre-extracted wood exhibited 15 and 29 wt-% reduction in the hemicellulose content for the DBU-butanol-CO_2-SIL and DBU-hexanol-CO_2-SIL, respectively. This result could be attributed to the lower viscosity of DBU-butanol-CO_2-SIL compared to DBU-hexanol-CO_2-SIL, which might be also causing an improved mass transfer of fluid in and out of the wood chip during SIL treatment. On the other hand, only a minor effect could be attributed to the absence of wood extractives on the dissolution efficiency of the SILs. This is an indication that there would not be any absolute need for the pre-extraction of the wood samples, if so desired. Moreover, *a priori* removal of the wood extractives did not influence the lignin removal. Both hexanol and butanol SILs were rather neutral in terms of lignin removal, since the treatment of spruce wood with either DBU-hexanol-CO_2-SIL or DBU-butanol-CO_2-SIL resulted in about 2 wt-% of the lignin in the undissolved wood, compared to native wood.

Table 2. The effect of wood extractives on wood dissolution

Wood	SIL	Weight reduction [wt%]	Reduction in the sugar content [wt%]
Dried native spruce wood	DBU-hexanol-CO_2-SIL	10	14
Dried native spruce wood	DBU-butanol-CO_2-SIL	13	36
Pre-extracted spruce wood	DBU-hexanol-CO_2-SIL	10	15
Pre-extracted spruce wood	DBU-butanol-CO_2-SIL	11	29

Treatment condition: 55 °C, without stirring under normal atmosphere, 5 days

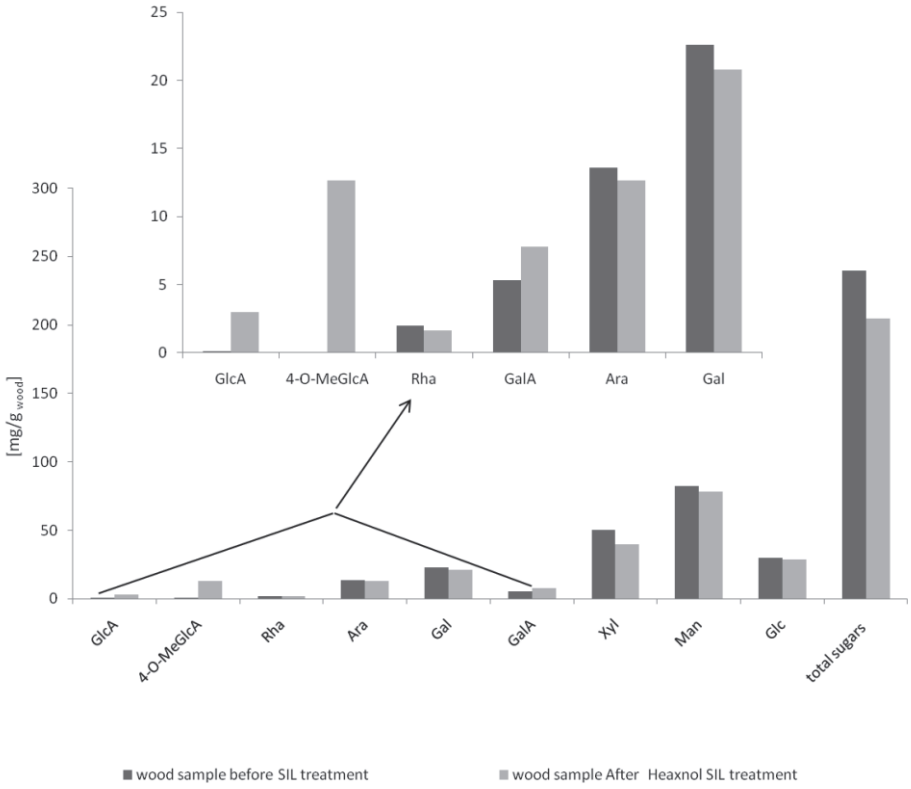


Figure 11. The total sugar content of wood sample before and after treatment with DBU-hexanol-CO_2-SIL at 55°C for 5 days, no stirring

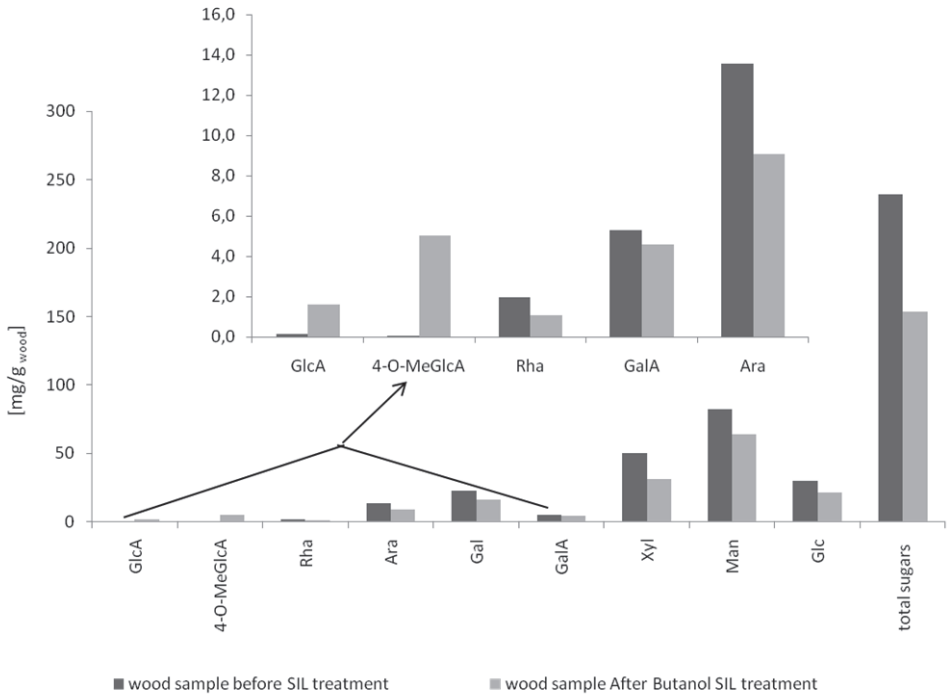


Figure 12. The total sugar content of wood sample before and after treatment with DBU-hexanol-CO_2-SIL at 55°C for 5 days, no stirring

Morphology of the samples investigated by SEM is presented in Fig. 13. It can be seen that after the pre-treatment of wood (*Picea abies* spruce) with DBU-hexanol-CO_2-SIL (Figure 13 b), the middle lamella becomes clear. This result indicates that the dissolution of pectin (also seen as galacturonic acid) occurs, together with a significant reduction of the sugar content in the wood sample.

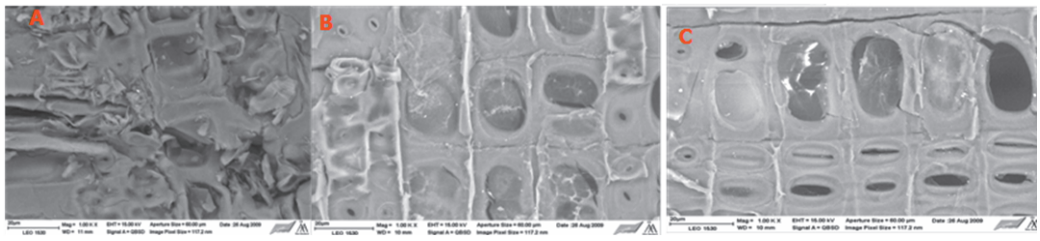


Figure 13. SEM images of the morphology, a. native Spruce wood, b. wood treated with DBU-hexanol-CO_2-SIL, 1 day and c. wood treated with DBU-hexanol-CO_2-SIL, 5 days the treatment was performed at 55 °C under normal atmosphere and pressure.

3.2.3. Influence of wood chip size

The influence of the wood chips size in terms of the dissolution was studied in order to see if any noticeable effect could be attributed to the milling of wood using SILs as solvents. The dissolution of wood flour with the size of about 350 μm was as expected to be more efficient than that performed with the larger wood chips (typical industrial chips of around 30 mm x 30 mm). More efficient fractionation was expected because of the increased external surface area and the prior mechanical breaking down of the internal structure of the wood chips occurring during the milling process. In fact, the milling process has been shown to decrease the crystallinity of wood material [48]. Furthermore, the amount of glucose observed after acid hydrolysis was reduced by 6 wt- % in case of the milled wood compared to the wood chips of the native spruce. It is assumed that the acid methanolysis process would not break down glucose in the cellulose fibers and, thus, the glucose after this treatment is mainly originating from hemicellulose [35, 36]. These result indicated that part of the cellulose was also dissolving during SIL treatment, when pre-milled wood was used as a raw material. The glucose amount in wood can be related to the amount of cellulose in the wood.

3.3. Treatment of birch wood with a switchable ionic liquid based on DBU-glycerol carbonate [IV]

The suitability of SILs as solvents for dissolution of lignocellulosic material was monitored by measuring the weight loss of the birch wood before and after SIL treatment. Fresh birch chips containing substantial amount of water were used upon this test. Drying of the wood requires additional energy input and is undesirable from the point of energy use. The birch chips used were industrial size chips (3 cm x 3 cm x 0.5 cm) and after 5 days of treatment with a SIL the chip weight was reduced by 25 % and over 50 % for the chip treated with DBU-glycerol-CO_2-SIL and DBU-glycerol-SO_2-SIL, respectively. The reductions in the hemicelluloses content of the chip were monitored mainly by performing acid methanolysis followed by GC- analysis of the undissolved chip after SIL treatment. Further, also an analysis of the recovered solid material from the spent SIL was carried out. The solid material recovered was mainly hemicellulose.

3.3.1. Undissolved residual from the DBU-glycerol-SILs treatment

The amounts of different components, both in native and undissolved wood samples and being treated with either DBU-glycerol-CO_2-SIL or DBU-glycerol-SO_2-SIL, are shown in Fig. 16. In the native birch, the main components were cellulose, hemicelluloses and lignin accounting for 41%, 33%, and 21% of the total mass, respectively. In addition, the remaining 5% was composed of mainly ash and extractives (Table 3). The undissolved wood residue contained also 53% and 76% cellulose, respectively, after being treated either with DBU-glycerol-CO_2-SIL or DBU-glycerol-SO_2-SIL. These results indicate that very pure cellulose fibres were produced when using DBU-glycerol-SO_2-SIL as a solvent for birch treatment. Furthermore, only low amounts of glucose were dissolved during the SIL treatment. Majority of xylan (21%) ended up in the liquid stream upon DBU-glycerol-CO_2-SIL treatment, corresponding to 76% of the original amount in the untreated wood. Unfortunately, no results on the amount of xylan in the liquid stream after DBU-glycerol-SO_2-SIL treatment were recorded. Furthermore, the undissolved solid (treated and washed wood) composed of only 2% lignin. In comparison, DBU-glycerol-CO_2-SIL treatment of birch chip removed 10% of xylan and 8% of lignin.

3.3.2. Mass balance during wood dissolution with switchable ionic liquids

By monitoring the process and making mass balances it was easy to confirm very low losses of material during handling and SIL treatment. The components of dissolved and undissolved wood samples after treatment, with either DBU-glycerol-CO_2-SIL or DBU-glycerol-SO_2-SIL, were plotted in the pie diagrams and compared with that of the native birch. DBU-glycerol-SO_2-SIL was in total able to dissolve 95% of the hemicelluloses in the wood. Also, the weight of the recovered, undissolved residuals was reduced by 50 wt-%, whereas only 25 wt-% was dissolved when using DBU-glycerol-CO_2-SIL as a solvent. The chemical compositions of the birch wood before and after SIL treatment, expressed in mg/g dry mass, are presented in Table 3. The main dissolved components are hemicelluloses pectin and extractives. The sugar content of the undissolved wood samples reduced with DBU-glycerol-CO_2-SIL and DBU-glycerol-SO_2-SIL to about 15 wt-% and 75 wt-%, respectively. The results indicate that DBU-glycerol-SO_2-SIL was much more efficient in dissolution of birch than DBU-glycerol-CO_2-SIL. The reasons might be the differences in acidity and, consequently, the acidity of the DBU-glycerol-

SO_2-SIL could be related to having same acidity (pKa~ -7) value with HCl while the acidity of the DBU-glycerol-CO_2-SIL could be related to that of trichloroacetic acid (pKa~0.77) [45].

Table 3. Chemical compositions of the birch wood before and after SIL treatment, expressed in mg/g dry mass

Sample	Cellulose [a]	hemicellulose	lignin	Total [b]
Native birch	412	333	207	952
DBU-glycerol-CO_2-SIL treated birch chip 24 h	398	287	186	871
DBU-glycerol-CO_2-SIL treated birch chip 120 h	553	251	185	989
DBU-glycerol-SO_2-SIL treated birch chip 120 h	790	24	<2	816
Recovered solid from spent DBU-glycerol-CO_2-SIL	38	276	N.D	

[a] the content has been calculated by excluding the average glucose amounts, multiplied by the factor of 0.9

[b] The values of extractives and ash of the birch wood chips are not included in the presented values

N.D. - not detected

3.3.3. Structure of the SIL treated birch

The morphology of the untreated birch wood chip is presented in Fig 14a whereas the SIL treated wood samples are presented in Fig.14b and c, respectively. The middle lamella became clearly visible after the treatment of wood (*Betula* birch chip) with the SILs, with DBU-glycerol -CO_2-SIL (Fig. 14b) and DBU-glycerol-SO_2-SIL (Figs. 14c and 15c). Furthermore, the undissolved wood samples being removed from the DBU-glycerol-SO_2-SIL were nearly completely fibrillated containing only small amounts of hemicelluloses and lignin. The total weight loss of the wood with DBU-glycerol-SO_2-SIL was about 95 wt-%. On the other hand, the fibrillation of the undissolved wood samples using DBU-glycerol-CO_2-SIL (Figs. 14b and Figure 15b) was not complete. In addition, the amount of hemicelluloses was reduced by 15 wt % only and the total weight loss was

25 %. These results together with the chemical analysis indicate that dissolution of hemicelluloses, lignin and pectin (galactouronic acid) occurred.

Figure 14. SEM images of the a) native birch wood, b) wood treated with DBU-glycerol-CO_2-SIL for 5 day and c) wood treated with DBU-glycerol-SO_2-SIL for 5 days dissolution, at 100°C under normal atmosphere and pressure.

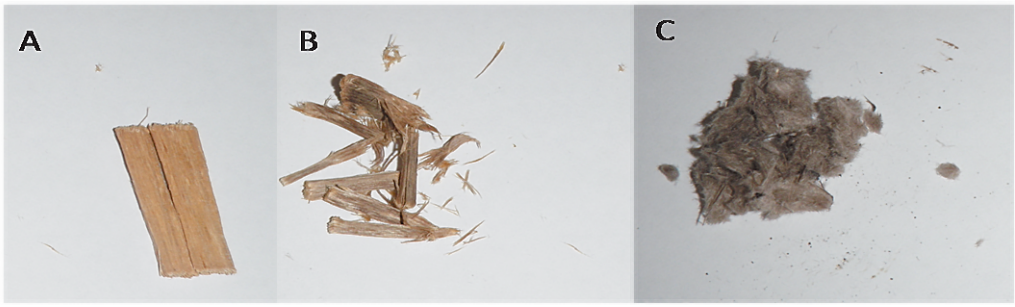


Figure 15. Photographs of the wood samples: a) native birch wood, b) wood treated with DBU-glycerol-CO_2-SIL and c) wood treated with DBU-glycerol-SO_2-SIL for 5 days at 100°C under normal atmosphere and pressure.

3.4. The influence of different parameters to dissolution capacity

3.4.1. Influence of dissolution time

The influence of time in terms of the dissolution capacity of the DBU-glycerol-CO_2-SIL on birch chips is shown in Fig. 16. As expected, better dissolution capacity was achieved with increased time. The weight reduction difference between a one day treatment and a five days treatment was about 15 wt-%. The dissolution occuring during the first 24 h was 5.2 fold, at a rate of 0.83 wt-%/ h, compared to that during 24-120 h corresponding to 0.16 wt-%/ h. Likewise, the hemicellulose dissolution takes mainly place after 16 h, since the sugar content decreased by 8% within the first 24 h when using DBU-glycerol-

CO_2-SIL, although the corresponding decrease in lignin amounts were 10 wt-% after 24 h and 21 wt-% after 120 h for DBU-glycerol-CO_2-SIL. Thus, it can be concluded that the hemicellulose dissolution occurs in the beginning of the treatment, while lignin dissolution occurs towards the latter part of the treatment cycle.

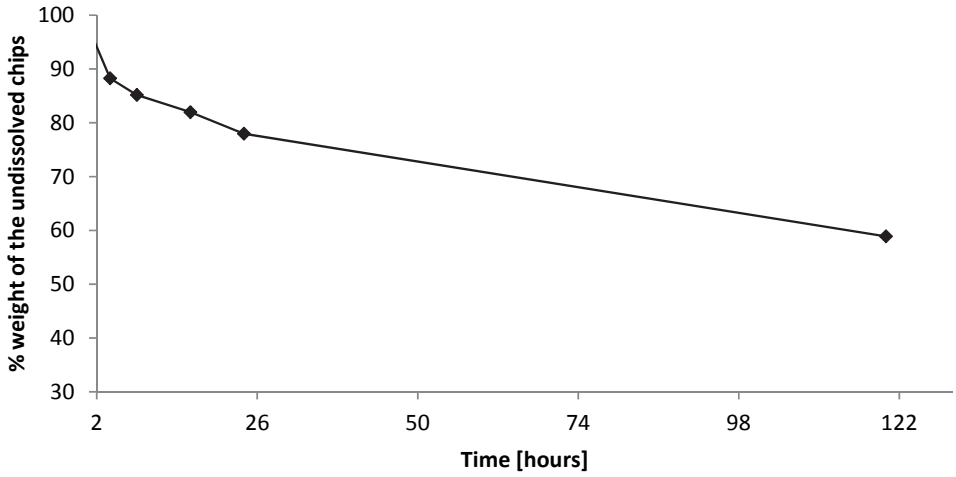


Figure 16. Time dependence of the dissolution of birch, with DBU-glycerol-CO_2-SIL at 100°C under normal pressure, from 1 to 5 days

3.4.2. Wood-to-SIL ratio

Only slight variations in the weight reduction of the wood after treatment with DBU-glycerol-CO_2-SIL, using various SIL-to-wood ratios were observed, paper **[IV]**. It should be pointed out that as little SIL should be used as possible in order to decrease the process costs.

3.4.3. Re-use of SIL

Spent SIL was used as a solvent for dissolution of fresh birch wood without any intermediate treatment steps before wood treatment. The reuse of spent SIL was demonstrated in four consecutive batches demonstrating only a slight reduction in the dissolution efficiency of the DBU-glycerol-CO_2-SIL, paper **[IV].** The fresh DBU-glycerol-CO_2-SIL exhibited about 9% better dissolution efficiency compared to the capacity of the spent DBU-glycerol-CO_2-SIL. The dissolution efficiency, nevertheless,

remained unaffected upon the next three consecutive reuses of the SIL, thus demonstrating that the reuse of SIL is feasible.

3.5. DBU-MEA-SIL as a delignification solvent for birch (*Betula Pendula*): switching with CO_2 vs. SO_2 [V]

3.5.1. DBU-MEA-CO_2-SIL and DBU-MEA-SO_2-SIL-treatments of milled birch

Selective fractionation of lignocellulosic material, i.e. milled birch wood, was facilitated in a SIL based on an alkanol amine, amidine and two types of acid gases (CO_2 or SO_2) at 120°C. The resulting fluffy material from the treatment can be compared to that obtained using typical pulping method before bleaching (Fig.17). The structural changes were minor when comparing the SEM images of the untreated wood and the wood treated with either SIL (Fig 18). The results revealed that 44% and 40% weight reduction were obtained after the treatment with the DBU-MEA-SO_2-SIL or DBU-MEA-CO_2-SIL, respectively.

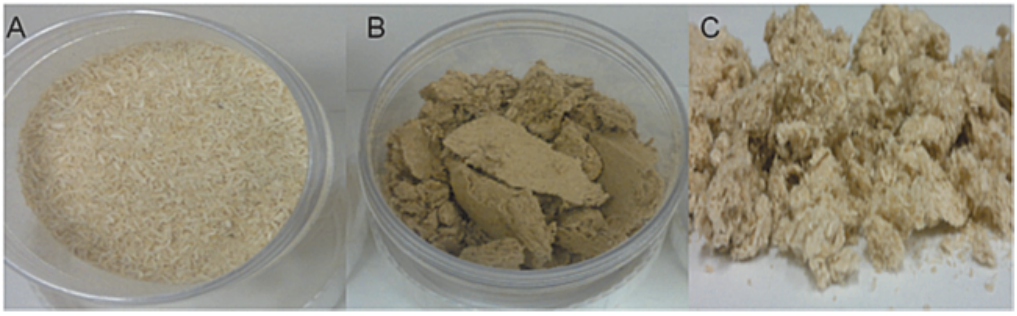


Figure 17. A) milled birch (~1 mm), B) MEA-CO_2-SIL treated birch C) MEA-SO_2-SIL treated birch, treatment was: 120°C for 24 h and with stirring.

Figure 18. SEM image presented are of magnification 1kx for A) milled birch (~1 mm) B) DBU-MEA-CO_2-SIL treated birch and C) DBU-MEA-SO_2-SIL treated birch. Treatment conditions: 120°C for 24 h and with stirring.

3.5.2. Chemical analysis

The undissolved wood material after SIL treatment was subjected to chemical analysis, to determine lignin, cellulose and hemicelluloses contents of the material, paper **[V]**. The SO_2 containing SIL was evidently more selective towards lignin dissolution compared to the CO_2 triggered SIL. The presence of SO_2 could be the reason, since comparable affinity toward lignin has been achieved using a sulfur containing ionic liquid [23, 27]. Regarding the removal of pectins and uronic acids, the results were quite similar for both SILs. Also, analogous results were achieved for the removal of the other wood sugars using both SILs. On the other hand, the glucose yield (cellulose content originating from cellulose hydrolysis in line with the analysis procedure) was much higher for the wood treated with DBU-MEA-SO_2-SIL (680 mg/g), resulting in higher glucose yield compared to both native wood and the DBU-MEA-CO_2-SIL treated wood whose yields were 420 mg/g and 660 mg/g, respectively. The SIL treatment facilitated removal of over 90 wt-% of the pectins and uronic acids from the wood. Furthermore, lignin was almost completely removed when the DBU-MEA-SO_2-SIL, whereas about 50 wt-% was removed upon treatment with the DBU-MEA-CO_2-SIL. Thus, it is evident that the DBU-MEA-SO_2-SIL was more selective towards lignin removal compared to the DBU-MEA-CO_2-SIL.

The recovered material from the spent SIL was precipitated using methanol (Figures 19A and B, respectively). It was found that the recovered materials are mainly composed of hemicelluloses, in addition to some of lignin. The recovered materials were lean in cellulose meaning that the SIL did not dissolve cellulose, but mainly lignin and hemicelluloses.

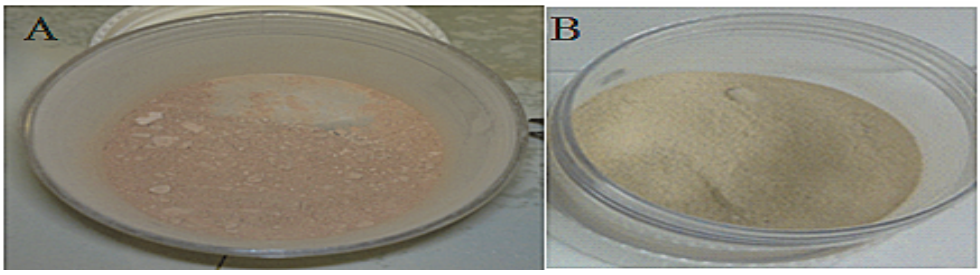


Figure 19 A) Recovered solid from DBU-MEA-SO_2-SIL treated birch treated birch, B) Recovered solid from DBU-MEA-CO_2-SIL treated birch, treatment conditions: 120°C for 24 h.

3.5.3. FT-IR of the undissolved treated wood

The spectra presented in paper **[V]** introduce native birch wood and treated birch using DBU-MEA-SO_2 SIL and DBU-MEA-CO_2 SIL. The strong absorption band at 3400 cm^{-1} due to O-H stretching was observed and the presence of the C-H stretching was observed at 2910 cm^{-1}. In addition, a number of distinct changes were observed on peaks at the finger-print region between 1800 and 600 cm^{-1} [49, 50]. The strong carbonyl band observed at 1740 cm^{-1} was attributed to the evidence of high hardwood xylan content [51]. However, a clear and well-marked reduction of the peak at 1740 cm^{-1} after treatment with SIL could also be seen. The peaks at 1650 and 1590 cm^{-1}, respectively, were assigned to absorbed O-H and conjugated C-O. Also, the aromatic skeleton displayed a reduced intensity. The reduction in the intensity of the peak at 1504 cm^{-1} was attributed to vibration of the aromatic skeleton [52] after SIL treatment further suggesting lignin removal.

3.5.4. Nuclear magnetic resonance (NMR) of the undissolved treated wood

^{13}C NMR spectra of the undissolved material after SIL treatment are shown together with a reference of native birch in Fig. 20. A signal assigned to cellulose is in the region between 50 and 105 ppm while the signal at 89 ppm relates to C-4 of the highly ordered cellulose of the crystallite interiors. On the other hand, the broader upfield signal at 84 ppm is assigned to the C-4 of disordered cellulose [53, 54]. The signals resonating at 21 and 173 ppm, respectively, denote the methyl and carboxylic carbon of acetyl groups attached to hemicelluloses and their intensities were reduced after both SO_2 and CO_2 based SIL treatment (Fig. 20), thus indicating the removal of hemicelluloses from the wood. An obvious reduction of the peak in the region between 125 and 160 ppm was observed and assigned mainly to the aromatic carbons of lignin, upon comparison of the spectra in Figure 20A (untreated birch) and Figure 20b/c (treated birch wood). Though the results from NMR can be considered as semi-quantitative, they can, nevertheless, be interpreted as to reflect the nearly complete removal of lignin from wood. Still, considerable amounts of the hemicelluloses were removed.

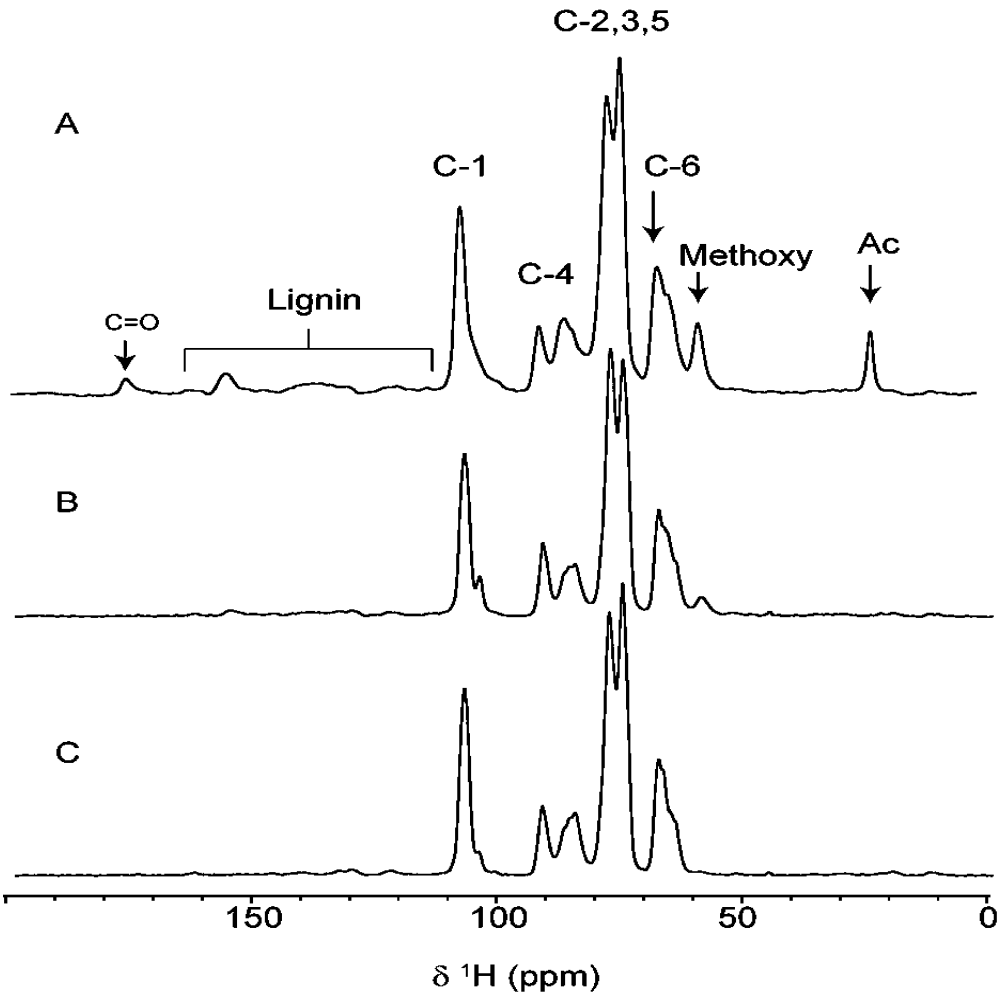


Figure 20. NMR spectra for A) milled birch (~1 mm), B) DBU-MEACO_2-SIL treated birch and C) DBU-MEASO_2-SIL treated birch, treatment conditions: 120°C for 24 h with stirring.

3.5.5. Gel permeation chromatography (GPC) analysis of the undissolved treated and untreated wood

The molecular weight distribution (MWD) of the carbohydrates for the native birch wood and the SIL treated samples were analyzed. Birch wood depicts a bimodal molecular weight distribution which originates from the hemicelluloses (low molecular weight region) and cellulose (high molar mass) as shown in Figure 21 (black curve). Assuming a Gaussian distribution of the single carbohydrate types, the MWD curve has been deconvoluted into the single compounds. Integration of the Gaussian curves provides the cellulose and hemicellulose content, respectively. The results are in excellent agreement

with the carbohydrate analysis performed with gas chromatography (GC). The MWD-curve of the DBU-MEA-CO_2-SIL treated residue also displays a bimodal distribution (Fig. 21, blue solid line). Though, the content of cellulose and hemicellulose were in disagreement with the carbohydrate analysis when deconvoluted. This indicates that the cellulose and hemicellulose cannot be described by simple Gaussian functions and, thus invalidates this deconvolution methodology. This might indicate that some carbohydrate degradation occurred, resulting in lower average molecular weight and causing an overlap with the hemicellulose. The cellulose depolymerization is even more suspectible and obvious for the DBU-MEA-SO_2-SIL treated residue (Fig. 21, red solid line). It seems that the high molecular weight fractions were entirely degraded resulting in the disappearance of the initial bimodal shape.

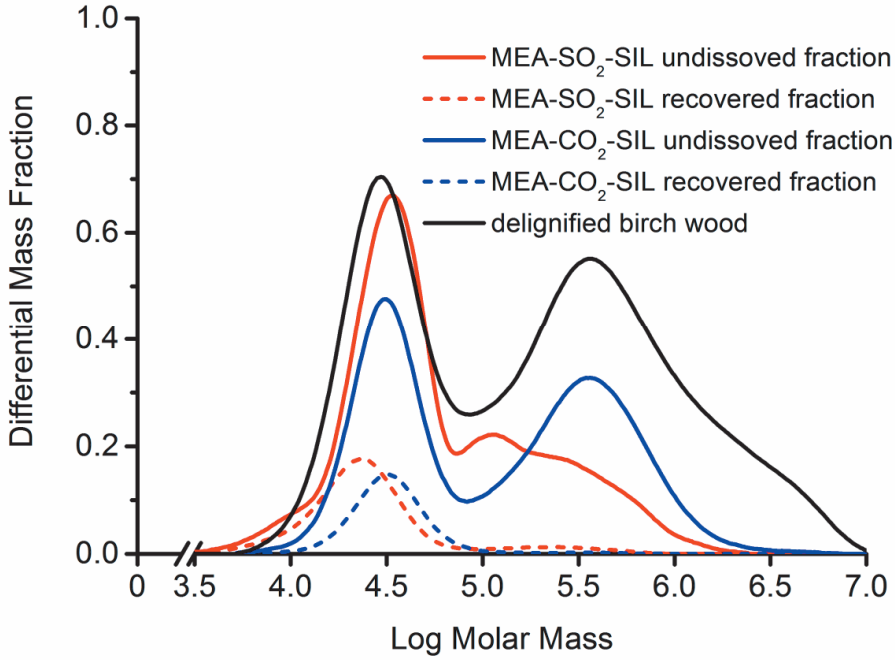


Figure 21. Molecular weight distribution of birch wood (black line), the undissolved residue (solid line), and the precipitated material (dashed line). MEA-SO_2-SIL: red, MEA-CO_2-SIL: blue. The curves have been weighted according the mass balances given in Table 7.

3.5.6. Short time high temperature (STHT) treatment using alkanol amine - superbase switchable ionic liquid systems as an optimal fractionation approach [VI]

Optimal conditions for a selective fractionation of lignocellulosic biomass in accordance to the short time high temperature treatment (STHT) using DBU-MEA-SO_2-SIL as a solvent was studied by measuring the weight loss of the woody biomass after SIL treatment. Upon use of air-dried industrial size chips (3 cm x 3 cm x 0.5 cm) and after 2 h of treatment with SIL at 160°C using a weight ratio of 1:3:5, wood-to-water-to-SIL (37 wt-% water), the chip weight was reduced by 35 wt-% and 30 wt-% for the birch and spruce chips, respectively. Upon addition of isopropyl alcohol the precipitated solid materials contained mostly lignin and about 10 wt-% and 25 wt-% hemicelluloses were recorded for spruce and birch, respectively.

3.5.6.1. Chemical analysis

The amounts of different components in the native and the undissolved wood samples being treated with DBU-MEA-SO_2-SIL are shown in Table 4. These results were obtained from the chemical analysis performed in this work (acid hydrolysis, acid methanolysis and Klason methods).

Table 4. The composition of the native and treated wood samples

Wood sample	Birch (*Betula pendula*)		Norway spruce *(Picea abies*)	
	Untreated (wt-%)	Treated (wt-%)	Untreated (wt-%)	Treated (wt-%)
Water content	<5		<5	
Components	Weight % on dry bases		Weight % on dry bases	
Extractive	4	N.D	4	N.D
Lignin	22	5	27	6
hemicelluloses	32	20	28	11
Cellulose	42	72	44	75
Total	100	97	100	92

The undissolved wood cellulose contents were 72 wt-% for the birch and 75 wt-% for spruce, respectively, after being treated with the SIL (Table 4). These results indicate that quite pure cellulose fibres were produced by the STHT treatment when using this SIL as

a solvent for wood treatment. Additionally, the majority of wood lignin (19 wt-% for birch and 18 wt-% for spruce, respectively) ended up in the liquid stream upon SIL treatment (lignin removal was over 95 wt-%) (Table 4).The undissolved birch wood material contained about 20 wt-% of hemicelluloses of which most of it was xylan; on the other hand, for the spruce sample the hemicelluloses were mainly glucomannan. In summary, the results presented indicate selective lignin removal in a short time using SIL as a solvent, and the main hemicelluloses that were removed were mainly pectins, thus, resulting in a hemicelluloses rich pulp as product (Figure 22).

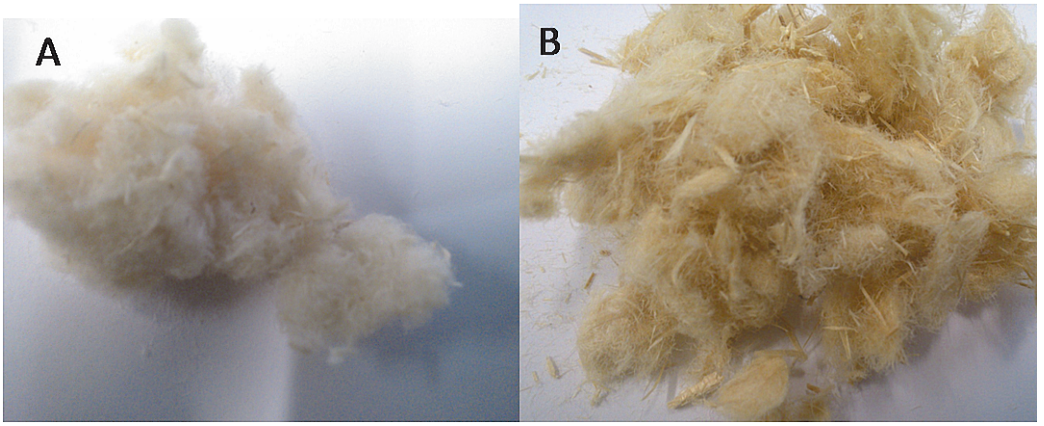


Figure 22. Undissolved fluffy material recovered from the STHT treatment for treatment of A) birch and B) spruce.

3.5.6.2. Carbohydrates qualitative analysis of the recovered residual by FTIR

The undissolved fractions of chips treated with the DBU-MEA-SO_2-SIL using the STHT treatment were analysed by FTIR. The results were compared to pure cellulose, treated birch, or with treated spruce. The absorbances at 3337–3362 (OH stretch), 2891–2896 (CH stretch), the bands at 1729, 1635/1641, 1155, 1028, and 895 cm^{-1} are associated with cellulose or hemicelluloses [62, 63] for the undissolved residual. The band at 1735 cm^{-1} comes from a C=O stretching vibration in acetyl groups of hemicellulose. This vibration band is consistent to hardwood species. The reduction in the intensities of the band at 1735 cm^{-1} in the undissolved residual treated with the SIL indicates that the dissolution of hemicelluloses occurred, and they are the main dissolved components in the dissolution of birch in SIL. The absorbance at 1164 and 895 cm^{-1},corresponding to C–O–C

asymmetric bridge stretching vibration in cellulose/hemicellulose and C–H deformation vibration in cellulose, respectively [62], were more resolved in both undissolved residual and the pure cellulose, thus indicating that the undissolved residual contains some carbohydrates. The characteristic peaks of lignin at 1590 cm^{-1} and at 1509 cm^{-1} were missing (C=C stretching vibration), whereas 1459 cm^{-1} (asymmetric bending in CH_3), 1419 cm^{-1} (C–H deformation), 1320 cm^{-1} , C–O vibration in the syringyl ring—not found in softwood lignin, as well as 1261/ 1231 cm^{-1} guaiacyl/syringyl ring and C–O stretching vibration [62, 64] were present in the spectra of the undissolved residues, indicating that the residue contained some lignin. It can thus be concluded that the undissolved residual after wood dissolution with the DBU-MEA-SO_2-SIL contained mostly cellulose with small amounts of hemicelluloses, since the peaks associated with hemicellulose have reduced intensities compared to those of the native wood. The spectra is shown in paper **[VI]**

3.5.6.3. Nuclear magnetic resonance (NMR) of the undissolved treated wood

^{13}C NMR spectra of the undissolved material after SIL treatment is shown together with a reference of native birch or native spruce respectively, in Fig. 23. The peaks assigned to cellulose are in the region between 64 and 105 ppm while lignin peaks are observed at 110-160 ppm (aromatic carbons) and 56 ppm (methoxy). The peaks from the acetyl group of acetylated hemicelluloses can be seen at 175 ppm (C=O) and 24 ppm (methyl) [53, 54, 65]. For the spruce sample, there was a distinct reduction in the amount of lignin and acetylated hemicellulose (peak at 24 ppm) after SIL treatment. However, the signals from the glucomannan back-bone are still quite noticeable after this treatment as there was still an intense signal peak at 104 ppm. Analogous results were found for the birch sample after SIL treatment where most of the lignin and the hemicellulose signals disappeared. Some residual hemicellulose, seen as a hump at the cellulose C1-peak at 105 ppm is still present, indicating that not all hemicelluloses were removed by the SIL treatment using the STHT system. Although the results from NMR technique can be said to be semi-quantitative, it is clear that this treatment leads to nearly complete removal of the lignin from the wood. Furthermore, considerable amounts of the pectins were removed.

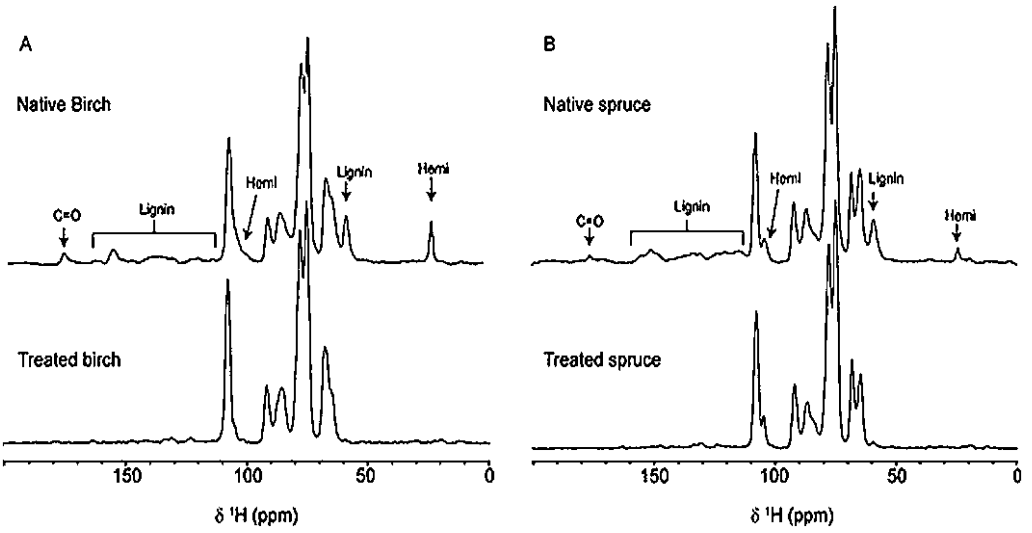


Figure 23. NMR spectra for ATop) birch (~3x3x0.5 cm), A bottom) DBU-MEA-SO_2-SIL treated birch and for B Top) spruce (~3x3x0.5 cm), B bottom) DBU-MEA-SO_2-SIL treated spruce, treatment conditions: STHT treatment (160°C for 2 h without stirring).

3.6. The composition and crystallinity of birch chips (*Betula Pendula*) upon 'DBU-DEA-CO_2 SIL' alkanol amine–organic superbase-derived SIL treatment [VII]

3.6.1. DBU-DEA-CO_2-SIL treatment of birch chips

A common practice when treating wood with IL is to mill the wood into fine flour [22, 23, 27]. In our earlier studies, native, industrial size birch chips were treated at 100°C in the absence of stirring and with a wood-to-SIL weight ratio of 1:5. A rather extensive removal of both lignin and hemicelluloses was achieved, though quite long treatment time (five days) was initially applied in the study. Similarly, native birch was treated using a slightly different SIL, whilst other conditions remained similar.

The weight reduction of the undissolved fraction of the wood chips after the SIL treatment was 20 wt-% after the first cycle, and the weight reduction recorded after the second SIL treatment cycle was 25 wt-%. The SIL treatment in this study reduced the wood lignin content by 27 wt-% of its original content in the native untreated wood after the 1st cycle. Upon the 2nd cycle of SIL treatment the lignin content was further reduced

by 6 wt-%. The SIL used for the second cycle was fresh and since not much more lignin was removed it can be concluded that it is a clear indication that the SIL affinity towards the lignin fraction was not very high. The trend in the hemicelluloses removal was similar as for the lignin removal, since the hemicelluloses content (sugars yield) was about 36 wt-% lower after two cycles compared to that of the native birch, whereas it was reduced by 18 wt-% after the first SIL treatment (Figure 24A-C). Upon addition of methanol to the spent SIL, the solid precipitates recovered were mainly hemicelluloses and about 90 wt-% of the material was xylose from methanolysis, as expected, since the treated wood was hardwood.

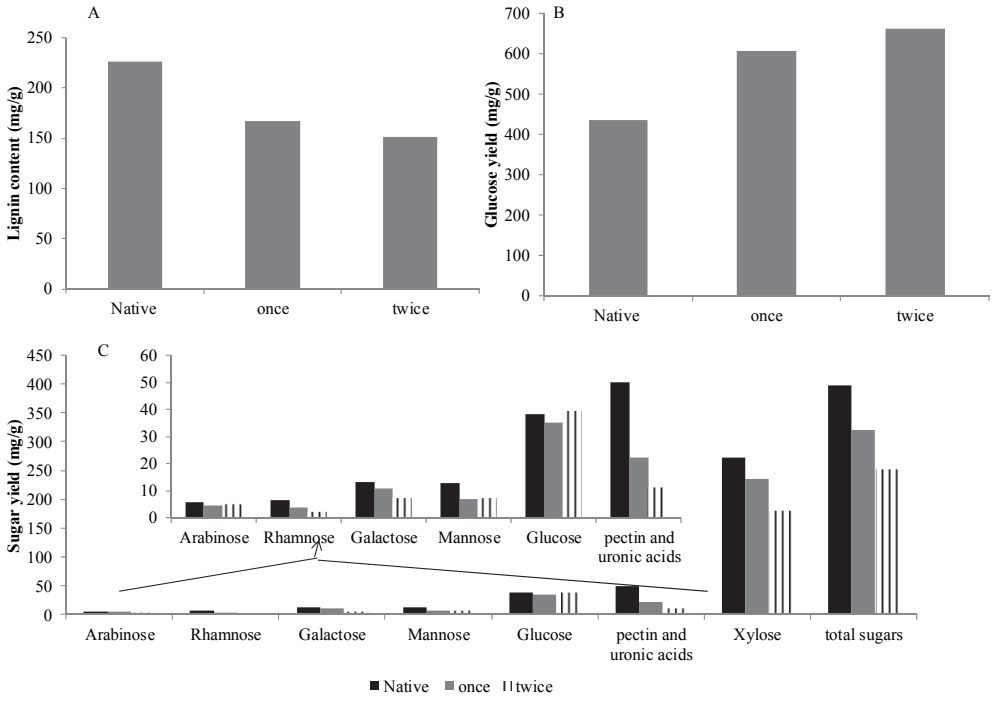


Figure 24. A) Lignin content B) cellulose content (glucose yield) and C) hemicelluloses content (sugar yield) for native birch chip and DBU-DEA-CO_2-SIL treated birch once and two twice treated, using fresh SIL in both treatments at 100°C for 24 h and in the absence of stirring.

3.6.2. XRD analysis of birch

The treatment of birch chips using DBU-DEA-CO_2-SIL resulted in a slight increase in crystallinity; however, lacking transformation of cellulose form I (Iα and Iβ) to form II,

which is a typically observed upon IL treatment of biomass [5, 55, 56]. The XRD patterns of untreated and DBU-DEA-CO_2-SIL treated wood chip samples are shown in Figure 31. In all three patterns, two major peaks (about at 15.8° and 22.1° 2θ) along with one weaker one (34.5° 2θ) were observed. These peaks originate from the cellulose form Iβ having monoclinic crystal system in and space group $P2_1$ with unit cell settings a = 7.784, b = 8.201, c = 10.38 and γ = 96.5° [57]. The strongest peak at 22.71° originates from the (200) lattice place and is indicative for d-spacing between the hydrogen bonded sheets. The second strongest broad peak at 15.8° is actually consisting of at least two overlapping peaks of form Iβ residing at 14.85° (-110) and 16.68° (110). All these peaks represent directions perpendicular to the fibre axis (c-axis), whereas the third clearly weaker peak at 34.54° (004) represents direction parallel to the fibre axis and is indicative for a quarter of the length of the cellobiose unit along c-axis. The crystallite diameter and length can be estimated using peak widths of the given peaks. The SIL treatment-induced changes can mainly be observed by comparing the XRD patterns of untreated and treated samples (Fig. 25). It can be seen that a major change has occurred on the baseline level between angular range of 10-20° 2θ, thus suggesting partial removal of amorphous content such as amorphous cellulose, lignin and hemicelluloses. The change is most significant between the untreated and once treated sample, whereas only minor differences exist between once and twice treated samples. When looking both once and twice treated XRD patterns (slightly more extensively on latter one), peak widths of the cellulose form Iβ seem to be tapered in to some extent, thus indicating either equal or slightly increased crystal size/crystallinity of cellulose form Iβ. In this particular case, one additional observation may suggest that slight crystallization of the crystallite zones may have occurred. By closely examining the peak position of the main peak at 22.1° in all three patterns, it is obvious that its position is shifted from 22.1° (untreated) via 22.2° (once treated) to 22.4° (twice treated) together with slight narrowing in the peak widths. This may indicate that the d-spacing between the sheets is shrunk and by this inducing slightly higher crystallinity. In addition, an increase in overall intensity and narrowing of the peak at 34.5° may evidence slight increase in length of the crystallite zones along the fibre axis. As already stated, a transformation from cellulose form I to form II is typically

observed during ‘classical’ IL and conventional solvent treatment of biomass and cellulose [24, 58-61]. However, herein, no evidence of transformation to form II can be seen, since the most likely observable moderately strong diffraction peak of form II at 12.2° (-110) is absent in both XRD patterns of the treated samples (Fig. 25). Thus, it can be postulated that this mild treatment of wood chips with SIL will retain the original cellulose forms instead of transforming them to the form II, whereas the more vigorous methods, like mercerization results in the transformation. The crystallinity of the SIL treated wood chips in our case, have either sustained or slightly increased the crystallinity of form I.

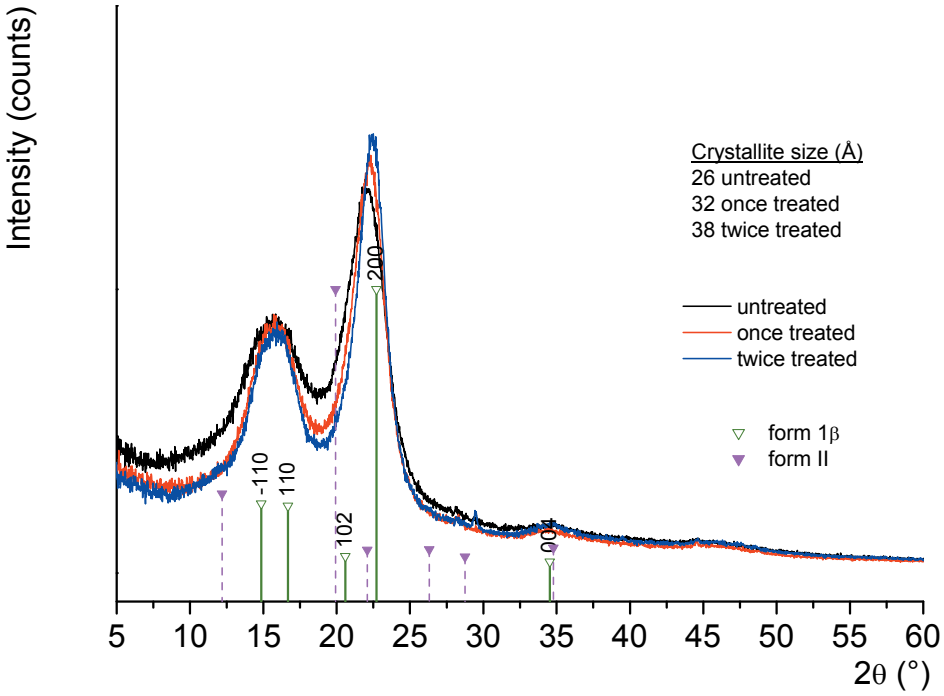


Figure 25. The XRD patterns of untreated, once and twice treated birch chip using DEA-CO_2 SIL. Fresh SIL was applied for the first as well as the second treatment at 100°C. The peak positions characteristics for cellulose form 1β21 are indicated by solid vertical lines with Miller indices. The peak positions of absent form II22 are shown with dashed vertical lines.

3.7. Comparison of the fractionation using SILs and conventional ILs for different wood species (selective fractionation vs. dissolution)

The dissolution efficiency of some ionic liquids has been presented comprehensively by Mäki-Arvela *et.al.* [22] Here the most interesting results are presented and compared with the results obtained using switchable ionic liquids. Furthermore, they are then compared with the SIL treatment using the STHT treatment. The nice results obtained for wood dissolution in 'classical' ionic liquids have been achieved by dissolving wood in [AMIM][Cl] [66] together with [EMIM][OAc] to obtain complete dissolution. Ionic liquids derived from polycyclic amidine bases, such as DBU, e.g. [HDBU] [Cl] were reported [64] to be capable to completely dissolve aspen wood chips [64]. 1-Allyl-3-methylimidazolium chloride was also reported to be capable to dissolve both hardwood and softwood wood chips. Only partial dissolution of Norway spruce was achieved in [AMIM][Cl] [28]. On the other hand, maple wood powder was dissolved in [AMIM][Cl] and in [BMIM][Cl] [4]. Also, three different types of wood chips, spruce, beech and chestnut were reported to have been completely dissolved in [EMIM][OAc]. Nonetheless, only a partial dissolution was achieved for silver fir (*Abies alba*) chips [14]. The results obtained after a dissolution period of 24 h, at 100°C of oak, eucalyptus, poplar and pine in a [BMIM][Cl/DMSOd6] as a solvent [67] revealed that about 67 wt% of cellulosic material and lignin were dissolved from poplar and pine, whereas slightly lower levels were achieved for eucalyptus and oak. In the case of the SILs, the result obtained for treating fresh birch wood (moisture content ~32 wt-%) at 100°C for 120 h under normal pressure and with the average chip size about 3 cm x 3 cm, about 25-52 wt-% weight reduction was achieved. Also, the result obtained upon treating fresh milled birch wood (moisture content ~32 wt-%) at 120°C for 24 h under normal pressure, with the average chip size about ca. 1 mm and with stirring, about 52 wt-% weight reduction was observed. There was a great improvement with regard to the treatment time, since the treatment time was reduced from 24 h to 2 h for both hard-and softwood. Also, the chips were of industrial size (3 cm x3 cm x 0.5 cm). Dissolution efficiency of wood in conventional ILs and SILs, is tabulated in ref. [22] and paper **[VI].**

4. CONCLUSIONS

Switchable Ionic Liquids (SILs) that could be thermally stable up to 200°C were synthesized. As an example, the mixture of glycerol and DBU was successfully converted from a molecular liquid mixture to an ionic liquid by bubbling CO_2 or SO_2 through it. The switching process is readily reversible since CO_2/SO_2 can be decoupled with a flow of N_2 and this process can be enhanced by heating the SIL to its decomposition temperature. FTIR spectra indicated that DBU was protonated via formation of N-H and $C{=}NH^+$ bands. NMR spectra of the SIL showed the formation of glyceryl carbonate. The DBU-glycerol-CO_2-SIL exhibited a viscosity increase from 0.96 PaS (molecular form) to 160 PaS (ionic form). The polarity change of DBU-glycerol-CO_2 system was visually demonstrated by the addition of Nile red dye, and a colour change from red to light yellow indicated the increase in polarity.

Selective extraction of hemicelluloses from spruce was demonstrated with SILs synthesised by bubbling CO_2 through a mixture of DBU and alcohols, at 55°C. With the DBU-hexanol-CO_2-SIL, the weight reduction of the milled spruce was 12 wt-%, while 4% weight reduction was recorded for chips. For the DBU-butanol-CO_2-SIL, the corresponding values were 10 wt-%, and 2 wt-%, reductions, respectively. The hemicellulose content was reduced by 38 wt-% for spruce treated with DBU-butanol-CO_2-SIL and by 29 wt-% for spruce treated with DBU-hexanol-CO_2-SIL. The SIL treatment was in reality not very efficient in terms of lignin removal, since the residual lignin fraction (extractives free wood) left in undissolved wood after SIL treatment were 16 and 20 wt-% of the total wood mass for the DBU-butanol-CO_2-SIL and DBU-hexanol-CO_2-SIL treated spruce, respectively. The non-extracted wood contained 22 wt-% lignin after treatment by both SIL.

SILs prepared from an amidine (DBU), glycerol and an acid gas, either SO_2 or CO_2, revealed to be efficient solvents for fresh birch chips. They tolerated moisture, could be regenerated, and reused without any precipitation in four consecutive cycles. The dissolution tests were performed using fresh birch wood at various dissolution times, at low temperature, 100°C, without stirring, under normal pressure. DBU-glycerol-SO_2-SIL

resulted in 56 % weight reduction on the birch wood, while there was about 25 % weight reduction on the birch wood treated with DBU-glycerol-CO_2-SIL. The differences in dissolution efficiencies of the SILs were associated to their acidity. The morphology of the undissolved birch wood treated with the DBU-glycerol-SO_2-SIL was much more fibrillated compared to that achieved by DBU-glycerol-CO_2-SIL treatment. The recyclability and reusability of the SILs was evaluated and the results revealed that the SILs can be reused upon wood dissolution, at least, up to four times. The dissolved components in the spent SIL were recovered upon addition of an anti-solvent.

The use of SIL as a solvent for the fractionation of birch (*B.pendula*) was also successfully demonstrated, using either DBU-MEA-CO_2-SIL or DBU-MEA-SO_2-SIL The undissolved material recovered after treating the milled birch wood with DBU-MEA-CO_2-SIL contained 60 wt-% cellulose, 12 wt-% hemicelluloses and 11 wt-% lignin, while the DBU-MEA-SO_2-SIL treated contained 80 wt-% cellulose 10 wt-% hemicelluloses and 4 wt-% lignin. These results indicated that over 50 wt-% and 80 wt-% lignin extraction was achieved using DBU-MEA-CO_2-SIL or DBU-MEA-SO_2-SIL, respectively. Furthermore, 90 wt-% of the wood pectin and uronic acids from the birch wood were dissolved. The treatment using either MEA-CO_2-SIL or MEA-SO_2-SIL resulted in 40 wt-% and 44 wt-% weight reduction, respectively, after 24 h treatment at 120°C, under vigorous agitation. The lignin extraction was also confirmed by NMR spectra since the signal between 160 ppm and 120 ppm assigned to lignin decreased after SIL treatment. The GPC results reveal less degradation of the cellulose by the treatment with DBU-MEA-CO_2-SIL compared to DBU-MEA-SO_2-SIL. Based on these results, by the choice of the acid gas upon SIL preparation, one can selectively extract components from birch wood, thus having almost pure fractions of the birch material. Simple solvent extraction can be applied to separate the dissolved fractions from the SIL.

Two-step treatment of birch chips containing ~5% moisture using DBU-DEA-CO_2-SIL with SIL-to-wood weight ratio of 5:1, at 100°C, in the absence of any agitation resulted in a reduction of 20 wt-% after the first treatment. In total, 25 wt-% reductions were recorded after the second treatment of the chip using fresh SIL. A 27 wt-% reduction in the lignin content was observed after the first cycle whereas a 29 wt-% reduction of the

wood lignin content was achieved after the second treatment step using fresh SIL. The XRD results indicated partial removal of amorphous material such as amorphous cellulose, lignin and hemicelluloses. The more significant changes were observed after the 1st treatment cycle of birch chips, whereas only minor differences were observed upon 2nd treatment cycle of birch chips fresh SIL.

The Short Time High Temperature (STHT) treatment for fractionation of wood biomass using DBU-MEA-SO_2-SIL, offers a selective and efficient way to extract components from lignocellulosic material. The undissolved wood treated with the SIL was fibrillated. A selective dissolution of mainly lignin was achieved by this system using SIL at 160°C for 2 h applying the STHT treatment. STHT was demonstrated to effectively fractionate both hard-and softwood into its major fractions, at a rather short time and using SIL water mixture as a solvent. About 95 wt-% of the lignin was extracted from the wood chips into the solvent. The dissolved components in the spent SIL were recovered by the addition of an anti-solvent. Over 70 wt-% of the dissolved components were recovered and 19 wt-% of it were hemicelluloses, while the rest of the material was in essence lignin. The undissolved fluffy material recovered after the treatment contained mainly a cellulose rich pulp, with ~70 wt-% cellulose and ~20 wt-% hemicellulose. The application of switchable ionic liquid prepared from an amidine (DBU), MEA and an acid gas, SO_2, was demonstrated as an efficient fractionation solvent for wood chips. In summary, we can conclude that switchable ionic liquids were proven as able fractionation solvent, working for various lignocellulose species and with tunable removal properties of lignocellulose constituents.

NOTATIONS

DBU	1,8-diazabicyclo-[5.4.0]-undec-7-ene
MEA	monoethanolamine
STHT	Short time high temperature
XRD	X-ray diffraction
DBN	1,5-Diazabicyclo[4.3.0]non-5-ene
DEA	diethanolamine
TMG	1,1,3,3-tetramethylguanidine
SIL	Switchable Ionic Liquid
FTIR	Fourier transform infrared spectroscopy
ATR	Atttenuated total reflectance
NMR	Nuclear magnetic resonance
[AMIM][Cl]	1-Allyl-3-methylimidazolium chloride
[BMIM][Cl]	1-butyl-3-methyl-imidazolium chloride
[EMIM][OAc]	1-ethyl-3-methyl-imidazolium acetate
[HDBU] [Cl]	1,8"-diazabicyclo[5.4.]undec"-7"-enium chloride
TGA	Thermo gravimetric analysis
SEM	Scanning electron microscopy
DSC	Differential scanning calorimetric
GPC	Gel permeation chromatography
EDA	ethylenediamine

LITERATURE CITED

[1] Wyman, C.E., Dale, B.E., Elander, R.T., Holtzapple, M., Ladisch, M.R., Lee, Y.Y. Comparative sugar recovery data from laboratory scale application of leading pretreatment technologies to corn stover. *Bioresource Technology,* **2005**, 2026-2036.

[2] Gomez, L.G., Steele-King, C.G., McQueen-Mason, S.J. Sustainable liquid biofuels from biomass: the writing's on the walls. *New Phytologist,* **2008**, 473-485.

[3] Li, C., Knierim, B., Manisseri, C., Arora, R., Scheller, H.V., Auer, M., Vogel, K.P., Simmons, B.A., Singh, S. Comparison of dilute acid and ionic liquid pretreatment of switchgrass: Biomass recalcitrance, delignification and enzymatic saccharification. *Biotechnology*,**2010**:4900-4906.

[4] Lee, S.H., Doherty, T.V., Linhardt, J.S. Ionic liquid-mediated selective extraction of lignin from wood leading to enhanced enzymatic cellulose hydrolysis. *Biotechnology and Bioengineering,* **2009**, 102 1368–1376.

[5] Sun, N., Rahman, M., Qin, Y., Maxim, M.L., Rodriguez, H., Rogers, R.D. Complete dissolution and partial delignification of wood in ionic liquid 1-ethyl-3-methylimidazolium acetate. *Green Chemistry,* **2009**, 646-655.

[6] Encyclopaedia of Chemical Technology. In Concise Encyclopaedia of Chemical Technology (Kirk-Othmer ed., vol. 1&2, Fifth Edition edition. New York: John Wiley & sons; **2007**.

[7] Sjöström, E. Wood Chemistry. Fundamentals and applications. New York: Academic press; **1993**.

[8] Klemm, D., Heublein, B., Fink, H.-P., Bohn, A. Cellulose: Fascinating biopolymer and sustainable raw material. *Angew Chem Int Ed,* **2005**, 3358-3393.

[9] Klemm, D., Philipp, T., Heinze, T., Heinze, U., Wagenknecht, W. Comprehensive cellulose chemistry vol.1, . Wiley-VCH, Chichester, **2005**.

[10] Pinkert, A., Marsh, K.N., Pang, S., Staiger, M.P. Ionic liquids and their interactions with cellulose. *Chemical Reviews,* **2009**, 6712-6728.

[11] Fengel. D., Wegener, E. Wood-Chemistry Ultrastructure Reaction. Berlin, New York: Walter de Gruyter; **1984**.

[12] Laine, C. Structures of hemicelluloses and pectins in wood and pulp. Helsinki University of Technology, Helsinki University of Technology, **2005**.

[13] Mäki-Arvela P, Salmi T, Holmbom B, Willför S, Murzin DY: Synthesis of rare sugars by hydrolysis of hemicelluloses – a review. *Chemical Reviews,* **2011**, 111.

[14] Zavrel, M., Bross, D., Funke, M., Buchs, J., Spiess, A.C. High-throughput screening for ionic liquids dissolving (lingo-) cellulose. *Bioresources Technology,* **2009**, 2580-2587.

[15] Huber, G.W., Iborra, S., Corma, A. Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering. *Chemical Reviews,* **2006**, 4044-4098.

[16] Kumar. P., Barrett, D., Delwiche, M.J., Stroeve, P. Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuels production. *Industrial & Engineering Chemistry Research*, **2009**, 3713-3729.

[17] Sun, Y., Cheng, J. Hydrolysis of lignocellulosic materials for ethanol production: a review. *Bioresource Technology,* **2002**, 1-11.

[18] Grous, W.R., Converse, A.O., Grethein, H.E. Effect of steam explosion pretreatment on pore size and enzymatic hydrolysis of poplar. *Enzyme and Microbial and Technology,* **1986**, 274-280.

[19] Mosier, N.S., Wyman, C., Dale, B., Elander, R., Lee, Y.Y., Holtzapple, M., Ladisch, M.R. Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresource Technology,* **2005**, 96: 673–686.

[20] Teymouri, F., Laureano-Perez, L., Alizadeh, H., Dale, B.E. Optimization of the ammonia fiber explosion (AFEX) treatment parameters for enzymatic hydrolysis of corn stover. *Bioresource Technology,* **2005**, 2014-2018.

[21] Zheng, Y., Lin, H.-M., Tsao, G.T. Pretreatment for cellulose hydrolysis by carbon dioxide explosion. *Biotechnology progress,* **1998**, 890-896.

[22] Mäki-Arvela, P., Anugwom, I., Virtanen, P., Sjöholm, R., Mikkola, J.-P. Dissolution of lignocellulosic materials and its constituents using ionic liquids-A review. Industrial Crops and Products, **2010**, 32:175-201.

[23] Tan, S.S.Y., MacFarlane, D.R., Upfar, J., Edye, L.A., Doherty, W.O.S., Patti, A.F., Pringle, J.M., Scott, J.L. Extraction of lignin from lignocellulose at

atmospheric pressure using alkylbenzenesulfonate ionic liquid. *Green Chemistry* **2009**, 11:339-345.

[24] Pinkert, A., Goeke, D.F., Marsh, K.N., Pang, S. Extracting wood lignin without dissolving or degrading cellulose investigations on the use of food additive-derived ionic liquids. *Green Chemistry* 2011:3124-3136.

[25] Swatloski, R.P., Spear, S.K., Holbrey, J.D., Rogers, R.D. Dissolution of cellose with ionic liquids. *Journal of American Chemical Society,* **2002**, 124:4974-4975.

[26] Wasserscheid, P., Welton, T. Ionic liquids in synthesis. Weinheim: Wiley-VCH; **2006**.

[27] Pu, Y., Jiang, N., Ragauskas, A. Ionic Liquid as a green solvent for lignin. *Journal of Wood Chemistry and Technology,* **2007**, 23-33.

[28] Kilpelainen, I., Xie, H., King, A., Granstrom, M., Heikkinen, S., Argyropoulus, D. Dissolution of wood in ionic liquids. *Journal of Agricultural and Food Chemistry,* **2007**, 55:9142–9148.

[29] Anugwom, I., Mäki-Arvela, P., Virtanen, P., Willför, S., Sjöholm, R., Mikkola, J.-P. Selective extraction of hemicellulose from spruce with Switchable Ionic liquids. *Carbohydrate Polymers,* **2011**, 87:2005-2011.

[30] Anugwom, I., Mäki-Arvela, P., Virtanen, P., Willför, S., Damlin, P., Hedenström, M., Mikkola, J.-P. Treating birch wood with a Switchable 1,8-diazabicyclo-[5.4.0]-undec-7-ene-glycerol Carbonate ionic liquid. *Holzforschung,* **2012**, 66:809-815

[31] Jessop, P.G., Heldebrant, D.J., Xiaowang, L., Eckert, C.A., Liotta, C.L. Reversible nonpolar to polar solvent. *Nature,* **2005**, 436:1102.

[32] Phan, L., Chiu, D., Heldebrant, D.J., Huttenhower, H., John, E., Xiaowang, L., Pollet, P., Wang, R., Eckert, C.A., Liotta, C.L., Jessop, P.G. Switchable solvents consisting of amidine /alcohol or guanidine/alcohol mixtures. *Industrial and Engineering Chemistry Research,* **2008**, 539-545.

[33] Anugwom, I., Mäki-Arvela, P., Virtanen, P., Damlin, P., Sjöholm, R., Mikkola, J.-P. Switchable Ionic liquids (SILs) based on glycerol and acid gases. *RSC Advances,* **2011**, 1:452-457.

[34] Neugebauer, H. In situ vibrational spectroscopy of conducting polymer electrodes. *Macromolecular Symposia,* **1995**, 61-73.

[35] Willför, S., Pranovich, A., Tamminen, T., Puls, J., Laine, C., Suurnäkki, A., Saake, B., Uotila, K., Simolin, H., Hemming, J., Holmbom, B. Carbohydrate analysis of plant materials with uronic acid-containing polysaccharides-A comparison between different hydrolysis and subsequent chromatographic analytical techniques. *Industrial Crops and Products,* **2009**, 29:571-580.

[36] Sundberg, A., Sundberg, K., Lillandt, C., Holmbom, B. Determination of hemicelluloses and pectins in wood and pulp fibers by acid methanolysis and gas chromatography. *Nordic Pulp and Paper Research Journal,* **1996**, 216-226.

[37] Schwanninger, M., Hinterstoisser, B. Klason Lignin: Modifications to Improve the Presicion of the standardized Determination. *Holzforschung,* **2002**, 56:161-166.

[38] Yeh, T.-F., Yamada, T., Capanema, E., Chang, H.-M., Chiang, V., Kadla, J.F. Rapid Screening of Wood Chemical Component Variations Using Transmittance Near-Infrared Spectroscopy. *Journal of Agricultural and Food Chemistry,* **2005**, 53:3328-3332.

[39] Yamamoto, M., Kuramae, R., Yanagisawa, M., Ishii, D., Isogai, A. Light-Scattering Analysis of Native Wood Holocelluloses Totally Dissolved in LiCl–DMI Solutions: High Probability of Branched Structures in Inherent Cellulose. *Biomacromolecules,* **2012**, 3982-3988.

[40] Nimz, H. Beech lignin-Proposal of a Constitutional scheme. *Angewandte Chemie International Edition in English,* **1974**, 13:313-321.

[41] Vishtal, A., Kraslawski, A. Challenges in Industrial Applications of technical Lignins. Bioresources, **2011**, 6:3547-3568.

[42] Brandt, A., Ray, M.J., To, T.Q., Leak D.J., Murphy, R.J., Welton, T. Ionic liquid pretreatment of lignocellulosic biomass with ionic liquid water mixtures. *Green Chemisty,* **2011**,2489-2499

[43] Shi, J., Gladden, J.M., Sathitsuksanoh, N., Kambam, P., Sandoval, L., Mitra, D., Zhang, S., George, A., Singer, S.W., Simmons, B.A., Singh, S. One-pot ionic

liquid pretreatment and saccharification of switchgrass. *Green Chemistry,* **2013**, 2579-2589.

[44] Heldebrant, D.J., Jessop, P.G., Thomas, C.A., Eckert, C.A., Liotta, C.L. The Reaction of 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) with Carbon Dioxide. *Journal of Organic Chemistry,* **2005,** 5335–5338.

[45] Heldebrant, D., Yonker, C.R., Jessop, P.G., Phan, L. Reversible Uptake of COS, CS_2, and SO_2: Ionic Liquids with O-Alkylxanthate, O-Alkylthiocarbonyl, and O-Alkylsulfite Anions. *Chemistry - A European Journal,* **2009**, 7619 – 7627.

[46] Silverstein, R.M., Bassler, G.C., Morrill, T.C. Spectrometric Identification of Organic Compounds. Fourth Edition edn: John Wiley & Sons; **1981**.

[47] Yu, T., Yamada, T., Gaviola, G.C., Weiss, R.G. Carbon Dioxide and Molecular Nitrogen as Switches between Ionic and Uncharged Room-Temperature Liquids Comprised of Amidines and Chiral Amino Alcohols. *Chemical Maters,* **2008**, 20 5337–5344.

[48] Zhao, H., Kwak, J.H., Wang,Y., Franz, J.A , White, M.J., Holladay, E.J. Effect of crystallinity on Dilute Acid Hydroylsis of Cellulose by Cellulose Ball-Malling Study. *Energy and Fuels,* **2006**, 807-811.

[49] Pandey, K.K., Pitman, A.J. FTIR studies of the changes in wood chemistry following decay by brown-rot and white-rot fungi. *International Biodeterioration and Biodegradation,* **2003**, 151-160.

[50] Hergbert, H.L. Infrared spectra of lignin and related compounds. II. Conifer lignin and model compound. *Journal of Organic Chemistry,* **1960**, 405.

[51] Bodîrlau, R., Teaca, C.A., Spiridon, I. Chemical Modification of Beech wood: Effect on Thermal Stability. *Bioresources,* **2008**, 3:789-800.

[52] Mohebby, B. Application of ATR Infrared Spectroscopy in Wood Acetylation. *Journal Agricultural Science Technology,* **2008**, 10:253-259.

[53] Maunu, S.L. NMR studies of wood and wood products. *Progress in Nuclear Magnetic Resonance Spectroscopy,* **2002**, 151-174.

[54] Wikberg, H., Maunu, S.L. Characterization of thermally modified hard-and softwoods by ^{13}C CPMAS NMR. *Carbohydrate Polymers,* **2004**, 461-466.

[55] Samayam, I.P., Schall, C.A. Saccharification of ionic liquid pretreated biomass with commercial enzyme mixtures. *Bioresource Technology,* **2010**, 101.

[56] Cheng, G., Varanasi, P., Li, C., Liu, H., Melnichenko, Y.B., Simmons, B.A., Kent, M.S., Singh, S. Transition of cellulose crystalline structure and surface morphology of biomass as function of ILs pretreatment and its relation to enzymatic hydrolysis. *Biomacromolecules,* **2011**, 933-941.

[57] Nishiyama, Y., Langan, P. Chanzy, H.J. Crystal structure and hydrogen-bonding system in cellulose Iβ from synchrotron x-ray and neutron fiber diffraction. *Journal of the American Chemical Society*, **2002**, 9074-9082.

[58] Thygesen, A., Oddershede, J., Lilholt, H., Thomsen, A.B., Ståhl, S. On the determination of crystallinity and cellulose content in plant fibres. *Cellulose,* **2005**, 563-576.

[59] Man, Z., Muhammad, N., Sarwono, A., Azmi, Bustam, M., Kumar, M.V., Rafiq, S. Preparation of Cellulose Nanocrystals Using an Ionic Liquid. *Journal of Polymers and the Environment***, 2011**, 726-731.

[60] Samayam, I.P., Hanson, B.L., Langan, P., Schall, C.A. Ionic-Liquid Induced Changes in Cellulose Structure Associated with Enhanced Biomass Hydrolysis. *Biomacromolecules*, **2011**, 3091-3098.

[61] Mansikkamäki, P., Lahtinen, M., Rissanen, K. Structural changes of cellulose crystallites induced by mercerisation in different solvent systems; determined by powder X-ray diffraction method. *Cellulose,* **2005**, 233-242.

[62] Labbé, N., Rials, T.G., Kelley, S.S., Cheng, Z.M., Kim, J.-Y., Li. Y. FT-IR imaging and pyrolysis-molecular beam mass spectrometry: new tools to investigate wood issues. *Journal of Wood Science Technology,* **2005**, 61–77.

[63] Liu, C.F., Sun. R.C., Zhang, A.P., Ren, J.L. Preparation of sugarcane bagasse cellulosic phthalate using an ionic liquid as reaction medium. *Carbohydrates Polymers,* **2007**, 17–25.

[64] D'Andola, G., Szarvas, L., Massonne, K., Stegmann, V. Ionic liquids for solubilizing polymers. WO 2008/043837, **2008**.

[65] Atalla RH, VanderHart DL: The role of solid state ^{13}C NMR spectroscopy in studies of the nature of native celluloses. Solid State Nuclear Magnetic Resonance **1999**, 1-19.

[66] Zavrel, M., Bross, D., Funke., M, Buchs., J., Spiess. A.C. High-throughput screening for ionic liquids dissolving (lingo-) cellulose. *Bioresources Technology,* **2009**, 2580-2587.

[67] Fort, D.A., Remsing, R.C., Swatloski, R.P., Moyna, P., Moyna, G., Rogers, R.D. Can ionic liquids dissolve wood? Processing and analysis of lignocelluloses materials with 1-n-butyl-3-methyl-imidazolium chloride. *Green Chemistry,* **2007**, 9:63–69.

ISBN 978-952-12-3030-1
Painosalama Oy – Turku, Finland 2014